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# ENGINEERING THERMODYNAMICS

BY

C. F. HIRSCHFELD

ASST. PROF. OF POWER ENGINEERING  
CORNELL UNIVERSITY

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Second Edition Revised and Corrected

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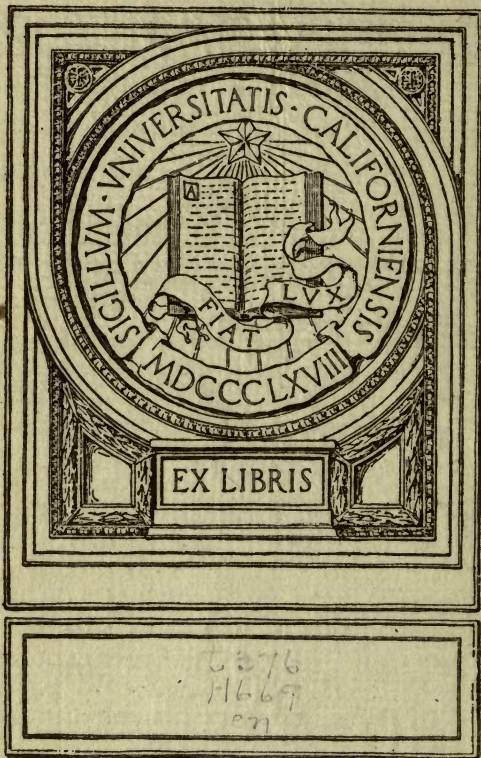


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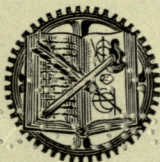
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## FOREWORD.

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THERMODYNAMICS is, like most other sciences, built upon and about a very small number of fundamental concepts. The average student, however, in his first attempts to obtain a working knowledge of this science is staggered by the enormous superstructure, and fails to observe and fix the few fundamentals upon which that superstructure rests.

The following pages represent an attempt to develop the principal Thermodynamic Properties of Gases and of Vapors in such a manner that the underlying principles may be clearly recognized. It is thought that a thorough understanding of the laws developed in the text

will, on the one hand, give a working knowledge sufficiently extensive for most engineering purposes, or, on the other, will enable the student to more easily follow the generalized and complicated cases considered in the large standard works on the subject.



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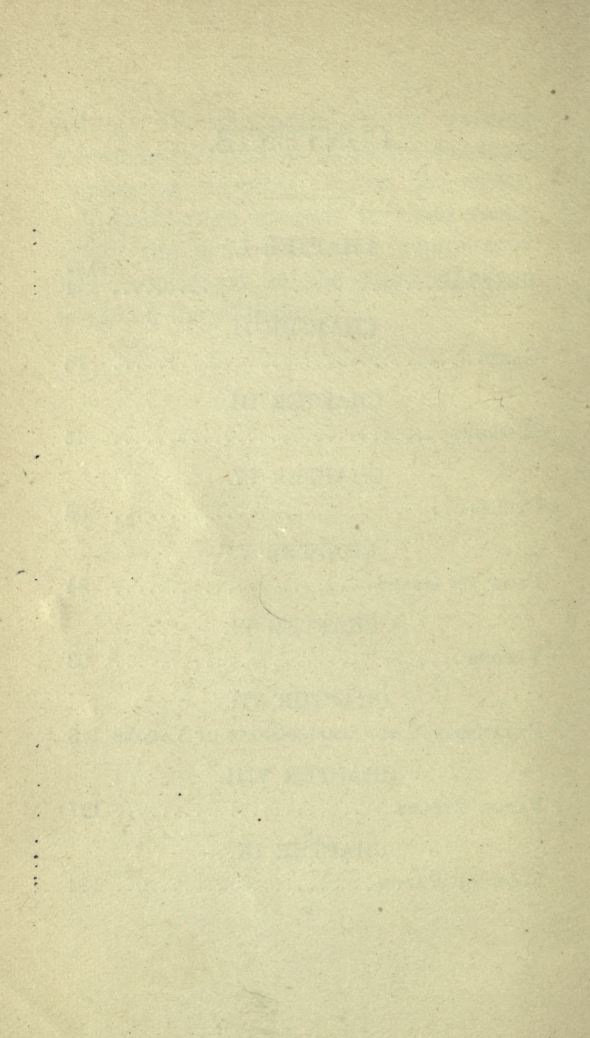
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# ENGINEERING THERMODYNAMICS.

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## CHAPTER I.

### HEAT.

THE historical experiments of Rumford and Joule proved heat to be a form of energy; and the work of practically all investigators in this field has shown the probability of heat being some form of molecular energy; that is, energy in some way connected with the motions and positions of the constituent particles of the various masses with which it is associated.

#### UNIT OF MEASUREMENT.

Heat as a form of energy may be measured in properly chosen units just

as any other form of energy may be measured. In practically all cases of energy measurement the units are based upon one or more of the effects produced upon a given body under given circumstances by the application of the particular form of energy considered. A rise in temperature is one of the most noticeable phenomena connected with an increase of heat, and, since it happens to be an effect the extent of which is comparatively easily measured, it is generally used as the one upon which to base the measurement of heat energy.

The unit used by engineers in English-speaking countries is called the British Thermal Unit and is defined in terms of the amount of heat required to cause a unit temperature change in a unit weight of water.

*Thus the British Thermal Unit (B.T.U.) is the quantity of heat required to raise the temperature of one pound of water one degree on the Fahrenheit scale.*

It has been discovered by experiment



that it requires different amounts of heat to produce this effect at different initial temperatures, and the unit is variously given for different points on the temperature scale. The most common is probably based upon a change of temperature from  $59^{\circ}$  to  $60^{\circ}$ . For exact determinations this temperature rise should be measured by means of a standard thermometer with gas for the expanding substance, but for all ordinary engineering purposes measurements may be made with a mercury thermometer. Further, the amount of heat per degree per pound may, for most engineering purposes, be considered constant at all points of the temperature scale.

#### FIRST LAW OF THERMODYNAMICS.

Experience has shown that by means of proper apparatus any form of energy can be converted into other forms, and that during this process absolutely nothing is lost. Heat energy and mechanical

energy are thus interconvertible and, since nothing is lost in the conversion, one unit of the one must always give a certain number of units of the other. The ratio of conversion has been determined by Joule and other experimenters, and the results of their work may be expressed as a law; thus, *Heat and Mechanical Energy may be converted the one into the other, and the ratio of conversion is approximately one heat-unit to 778 mechanical units.*

That is:

$$1 \text{ B.T.U.} = 778 \text{ foot-pounds.} \quad (1)$$

The value 778 is called Joule's equivalent and is represented by  $J$ . This law is generally called the "First Law of Thermodynamics."

It is a very simple matter to completely convert mechanical energy into heat energy, as is exemplified in the heat generated by friction of moving bodies and in other similar phenomena, but the change in the opposite direction is by far

more difficult of accomplishment. As will be seen later, the apparatus necessary to convert heat into mechanical forms of energy is complicated and at best does not even theoretically convert all of the heat energy supplied it. That which is converted gives of course 778 foot-pounds per unit, but much of it is rejected by the apparatus still in the form of heat, and, what is worse, under such conditions as to be waste heat.

## SECOND LAW OF THERMODYNAMICS.

Study of all the known heat phenomena of the universe has shown that *heat passes readily from bodies of high temperature to bodies of low temperature, but that external energy of some kind is necessary to make it pass in the reverse direction.* So important is this fact that it is called the "Second Law of Thermodynamics."

## HEAT-ENGINES.

The apparatus previously mentioned for the conversion of heat into mechanical

forms of energy takes various shapes, dependent upon the circumstances of its use, but they may all be called Heat-engines. They are of particular importance in the economics of this world, because, while man finds immense stores of heat tied up in latent form in the various fuels and easily liberated by the chemical processes of combustion, the mechanical motion necessary in his various industries does not occur just where and in just the manner needed. He is therefore driven by necessity to convert that which he has into that which he requires and he does it in some form of heat-engine.

The theoretical performances of these heat-engines are studied by means of the laws of Thermodynamics, a science built upon the two laws just given. It has for its object the determination of all the phenomena connected with the transformations of heat into mechanical energy and *vice versa*. The conversion taking place in all heat-engines depends upon the



behavior of various materials when subjected to different kinds of heat treatment. These materials are called working substances and are usually contained in some sort of confining vessels with proper mechanism to transmit the motions which they make available. They are generally gaseous substances for practical reasons, though so far as the theoretical side of the operations is concerned they might be solid, liquid, or gaseous.

#### DISTRIBUTION OF HEAT ENERGY ASSOCIATED WITH ANY SUBSTANCE.

It is a matter of common experience that when substances are heated various phenomena take place: temperatures rise, volumes change, solids melt, liquids vaporize, and all sorts of other familiar changes occur. When these are all studied side by side it is found that the results of changing the amount of heat associated with any substance may be grouped under three heads, irrespective of what its

characteristics are and what changes it may experience, provided it is not set in motion as a whole:

1. The temperature may change, described as a change of Sensible Heat.
2. Change may take place within the substance, necessitating the doing of Internal Work of a positive or negative character against internal forces. This would mean the absorption or giving out of heat energy equivalent to work represented by the change.
3. The volume may change with a corresponding displacement of the surrounding or inclosing medium, necessitating the doing of External Work of a positive or negative character and the transfer of an equivalent amount of heat.

These may be easily pictured mentally if a body of any kind be assumed to be made up of molecules in rapid motion and under certain circumstances exerting some sort of interattraction. Then a change

of temperature may be imagined as a change in the speed of vibration of the molecules—faster motion meaning higher temperature. An internal change may be imagined as a change of distance between the molecules, necessitating a supply of energy to overcome their interattraction when they are moved apart, and a supply of energy being liberated when they are allowed to approach.

The change of volume so far as external or enveloping media are concerned will mean simply that these media are displaced under whatever pressure they exert upon the surfaces of the body changing size. Since this means motion under a certain definite pressure, work is done. When the motion is such as to oppose the pressure, energy is absorbed, and energy is liberated when motion is in the same direction as the pressures exerted by the surrounding media. That is, when the volume increases, energy is absorbed to displace the enveloping medium. When the volume changes from large to small,

energy is given out to the same extent as it was absorbed at some previous time when the volume attained the larger value.

Since these changes are due only to the change of the amount of heat associated with the substance, the sum of all the energy changes must represent the amount of heat change; thus, algebraically,

$$Q = S + I + E, \quad (2)$$

where  $Q$  = amount of heat absorbed or given out, and, according to the molecular theory,

$S$  = the amount of heat necessary to make the molecules move faster when a rise in temperature takes place, or the amount given out when their motion becomes less rapid during a drop of temperature;

$I$  = amount of energy absorbed or given out by internal changes of molecular distances;

$E$  = amount of energy absorbed or given out by the external



media during an increase or decrease of the volume of the substance under consideration.

Since the amounts of energy represented by  $S$  and  $I$  are really stored within a substance when heated, the total amounts of such energy present in the body are called its intrinsic energy. Then  $S+I$  in a change may be called the change of intrinsic energy.

It should be clearly understood that under certain circumstances all of these energy changes may not occur, while under other conditions some may be positive while others are negative. Whatever the conditions, unless the condition of motion of the body as a whole is changed, expression (2) is always true if the proper signs and numerical values be used. This idea of the triple use of heat will become more evident and take on more meaning as the subject is further developed.

## SPECIFIC HEAT.

Equation (2) shows that if a substance is caused to undergo a certain change by the addition of heat, the amount of heat required to cause that change in the same body will always be the same, just as, in any other kind of a change which takes place in the universe, it always takes the same amount of energy to do the same amount of work. It is convenient to have names for the amounts of heat required to cause a unit amount of change of various kinds, and these are called thermal capacities. Thus there is a thermal capacity for unit rise in temperature, and this is commonly called the Specific Heat. Similarly, there is a thermal capacity for unit change of volume and it is commonly called the Latent Heat of Expansion. There are several other thermal capacities, but they are of minor importance and have no commonly accepted names.

As just indicated, *the Specific Heat of a*

*body is the amount required to cause unit temperature change in unit weight, and, if the specific heat is constant at all temperatures,*

$$\frac{Q}{W(T_2 - T_1)} = C, \quad (3)$$

where  $T_2$  and  $T_1$  represent final and initial temperatures;

$W$  = weight of substance in pounds;

and  $C$  = Specific Heat.

This expression may be written

$$Q = CW(T_2 - T_1); \quad (4)$$

and if the specific heat is variable, then

$$Q = W \int_{T_1}^{T_2} C dT. \quad (5)$$

From equation (2) it can be seen that it would be possible for  $Q$  to have different values for the same change in temperature if that temperature change could be accompanied by different amounts of internal and external work. Therefore

in equation (4) the value of  $C$  may vary with the conditions of heating; that is, the value of the specific heat may vary according to the conditions of heating, and every substance may have several specific heats. This is actually the case, as will be shown in the development of the equations for the behavior of gases.

Of all the numerous possible values for the specific heat of any single substance, it would seem possible to find one which represented the heat necessary to cause a change in  $S$  only. That is, one which represents the quantity of heat necessary to cause a change of temperature without any other heat-absorbing phenomena. Such a one would be called the True Specific Heat and would represent only the heat necessary to increase the velocity of vibration of the molecules during a rise in temperature of one degree. Such a specific heat will be considered in dealing with gases.

## EXTERNAL WORK DURING VOLUME CHANGES.

It is often necessary or desirable for purposes of analysis to divide the heat associated with changes in the condition of a body; that is to say, how much of it represents change of sensible heat, how much represents internal work, and how much external work. For this purpose an expression for the value of the external work is very necessary, and such an expression may be easily developed.

Assume any substance enclosed, as in Fig. 1, in the end of a cylinder behind

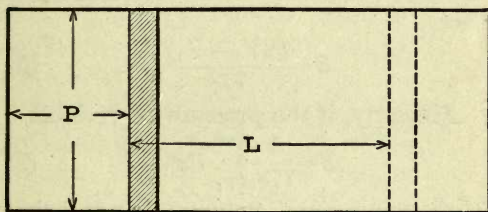


FIG. 1.

a moving piston of area  $a$  square feet and under a pressure of  $P$  pounds per



square foot. If the body be allowed to expand while the pressure is maintained constant, it will drive the piston out through a distance which may be called  $L$  feet. The expanding substance will then be doing external work, that is, work upon the confining piston, and the value of the external work in B.T.U. will be

$$E = \frac{aPL}{778};$$

but  $aL$  is the volume through which the piston moves, that is, the change of volume of the expanding substance, and if  $V_1$  and  $V_2$  be initial and final volumes in cubic feet,

$$E = \frac{P(V_2 - V_1)}{778}. \quad (6)$$

Similarly, if the pressure be variable,

$$E = \frac{1}{778} \int_{V_1}^{V_2} P dV, \quad (7)$$

each infinitesimal volume change being multiplied by the pressure existing while it took place and then all the small values of  $E$  being added together.

It is readily seen that equations (6) and (7) will apply equally well to cases where the volume change takes place in all three possible directions and they are therefore expressions for external work done during any kind of volume changes.

## CHAPTER II.

### GASES.

EXPERIMENTAL investigations into the behavior of gases under different conditions show that they all approximately obey very simple laws. None of them exactly obey these laws, but the farther the gases are removed from their points of liquefaction the nearer do the laws express their characteristics. Such being the case, it has become customary to consider an ideal "Perfect Gas" and to develop the laws which it would obey, and then so far as necessary to study the variations of the real gases from those laws. For all practical engineering purposes all of the ordinary so-called "permanent gases" may be assumed as perfect gases.

## LAWS OF THE PERFECT GAS.

A Perfect Gas may be defined as a substance existing in such a physical state that its constituent particles (molecules) exert no interattraction. Such a body would perfectly obey the laws of Boyle and Charles.

Boyle's Law states that *when the temperature of a gas is constant, its volume will vary inversely as the pressure upon it; that is,*

$$\frac{V_1}{V_2} = \frac{P_2}{P_1}, \quad (8)$$

or  $V_1 P_1 = P_2 V_2 = \text{a constant.} \quad (9)$

Charles' Law states that *with the pressure or the volume constant, the volume or the pressure of a gas will vary  $\frac{1}{493}$  of its volume at 32° F. for every Fahrenheit degree change of temperature, increasing in volume or pressure when the temperature increases.* If a gas be imagined with unit volume at 32° F., it would lose  $\frac{1}{493}$  part of that volume for every degree drop in tempera-

ture at constant pressure, and when it had dropped 493 degrees it would have zero volume if the law held at such low temperatures.

Such a point on the temperature scale, which is  $(493 - 32 = )$  461 degrees below the Fahrenheit zero, is called the Absolute Zero, and temperatures measured from it are called Absolute Temperatures. If the absolute temperature be represented by  $T$ , Charles' Law may be very simply stated in algebraic form:

When pressure is constant,

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}; \quad (10)$$

When volume is constant,

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}. \quad (11)$$

This idea of absolute temperature is very useful in dealing with heat-engines. The absolute temperature of a body in Fahrenheit degrees may be obtained from



the ordinary temperature above Fahrenheit zero by adding 461:

$$T = t + 461. \quad (12)$$

Apparently if real gases obey the law of Charles, they would have no volume at the temperature of absolute zero, but this absurdity need not be considered because they would all liquefy before reaching such a low temperature. That is, they would cease to even approximately obey the law which leads to this absurdity.

Boyle's and Charles' Laws may be combined to give a third and more general Law of Perfect Gases. If a volume of gas,  $V_1$ , at pressure  $P_1$  and temperature  $T_1$  have its temperature maintained constant while its pressure is changed to  $P'$ , its new volume,  $V'$ , will be given by equation (8):

$$V' = \frac{P_1 V_1}{P'}. \quad (13)$$

If then its pressure be kept constant while its temperature is varied to  $T_2$ ,

its new volume,  $V_2$ , will be given by equation (10):

$$V_2 = \frac{V'T_2}{T_1}; \quad (14)$$

and substituting for  $V'$  from (13),

$$V_2 = \frac{P_1 V_1 T_2}{P' T_1}. \quad (15)$$

Since  $P'$  is the same as  $P_2$ , an expression is derived which gives the value of the volume change for variations of both temperature and pressure:

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}, \quad (16)$$

which may be written

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \text{ or } \frac{PV}{T} = \text{a constant.} \quad (17)$$

Where the value of  $V$  above is for one pound of gas, the constant is called  $R$ , and this gives

$$\frac{PV}{T} = R. \quad (18)$$

Any of the equations under (17) or (18) is called the Law of Perfect Gases.

#### SPECIFIC HEAT OF PERFECT GASES.

A material constituted as is this ideal gas offers absolutely no resistance to separation of its constituent particles, since they exert no attraction upon one another, and therefore when it is heated no energy is absorbed for the purpose of doing internal work.

Hence in this case one pound of material when heated would require an amount of heat

$$Q = S + (I = 0) + E. \quad (19)$$

If such material is heated at constant volume, the pressure rises directly as the absolute temperature, as shown by the law of perfect gases, but no external work is done because the enveloping medium is not displaced, and under such conditions

$$Q = S. \quad (20)$$

In such a case the "Real or True " Specific Heat can be found by dividing  $Q$  by the change of temperature, provided that specific heat is constant with variable pressure and variable temperature. If it varies, the quotient will only be the average real specific heat.

The specific heat obtained under the conditions of constant volume as above is designated by  $C_v$  when expressed in Thermal Units, and by  $K_v$  when expressed in foot-pounds. Then

$$778C_v = K_v. \quad (21)$$

In the case of the ideal gas there is no theoretical reason why  $C_v$  should not be constant, that is, why it should not require exactly the same amount of heat to raise the temperature of one pound of a given gas one degree with volume constant no matter what the temperature, pressure, and volume.

If this quantity,  $C_v$ , obtained by dividing  $S$  by the change of temperature of

the body while receiving heat  $S$ , is a constant, it follows that the total sensible heat or intrinsic energy possessed by a gas must depend upon its temperature only. Thus if a gas have its temperature increased  $n$  degrees, its intrinsic energy will have been increased by  $nC_v$  heat-units, and if it have its temperature increased  $n'$  degrees, its sensible heat or intrinsic energy is increased by  $n'C_v$  heat-units. That the intrinsic energy of real gases may be considered to depend upon temperature only, and to be independent of volume and pressure, is shown by an experiment devised and performed by Joule and Thomson.

Their experiment was performed by means of two vessels connected by a passage containing a valve. One vessel was filled with gas at high pressure and the other was devoid of material content, that is, contained a vacuum. These two vessels were immersed in a larger vessel containing water, and when everything had reached the same temperature, the



valve between the two was opened so that the gas expanded in volume until it filled both vessels at an equal but lower pressure. Thermometers showed that no heat was given to or taken from the surrounding water, that is, the gas neither lost nor gained energy, and that after equilibrium had been established the temperature of the gas within the two vessels was sensibly what it had been when occupying only one vessel at a higher pressure.

*Here, then, was a change of pressure and volume with no loss or gain of heat energy by the gas within the vessel and the temperature remaining constant. It should be noted that no energy could have been lost by the doing of external work because under the circumstances the gas could do none. It therefore requires exactly the same amount of sensible heat or intrinsic energy to maintain a certain temperature no matter what the pressure and volume, and therefore the intrinsic energy of a gas may be said to depend upon the tempera-*

*ture only and to be independent of pressure and volume.*

In describing this experiment the temperature before and after expansion was said to be "sensibly the same," and advisedly. Very accurate measurements showed slight variations of temperature with the different gases tested, because in actual gases the molecules do exert interattractions. The experiments when considered with others of similar nature indicated, however, that these temperature changes would disappear when the attractions disappeared.

If one pound of gas be heated in such a way that the pressure remains constant, the volume increases directly as the absolute temperature,  $T$ . Increase of volume under external pressure means the doing of external work, and the heat necessary to cause a change of temperature under these conditions will be

$$Q = S + E. \quad (22)$$

For a given temperature range the

specific heat may be found by dividing  $Q$  by the temperature range, providing that specific heat be constant. If it is not constant, the quotient as before would be its average value through the particular temperature range chosen. The specific heat under constant pressure conditions is designated by  $C_p$  when measured in thermal units, and by  $K_p$  when measured in mechanical units. Then

$$778C_p = K_p. \quad (23)$$

Since the value of  $Q$  given by equation (22) is larger than the value of  $Q$  given by equation (20) by just the amount of the external work done, it is immediately seen that the specific heat at constant pressure is greater than the specific heat at constant volume by the amount of external work done by volume increase in the first case. This is easily seen to be so by imagining a change of one degree in temperature under the two different conditions. Then if the material being heated weighs exactly one pound, the

quantity of heat,  $Q$ , is the specific heat in each case.

$$C_p - C_v = E \text{ expressed in thermal units (24)}$$

and

$$K_p - K_v = \int_{V_1}^{V_2} P dV = P(V_2 - V_1). \quad (25)$$

The fact that  $C_p$  may be taken as practically constant, that is, independent of the pressure, for the ordinary gases has been proved by experiment, and it can readily be seen that it must be constant for the perfect gas by the following line of reasoning.

$C_p$  is larger than the constant  $C_v$  by just the amount of the external work done during a change of temperature, and since the value of  $C_v$  is the same for any one particular gas no matter what the pressure, the value of  $C_p$  must be independent of the pressure if it can be shown that the external work done in raising the temperature from a value  $T_1$  to a value  $T_2$  is the same at any two different pressures.

If a pound of gas be assumed to have a volume  $V_1$  at pressure  $P_1$  and temperature  $T_1$ , and to have a volume  $V_1'$  at pressure  $P_1'$  but the same temperature  $T_1$ , and if in both cases the temperature be raised to  $T_2$  while the pressure remains constant, Boyle's Law gives

$$P_1 V_1 = P_1' V_1' \text{ at temperature } T_1, \quad (27)$$

and

$$P_1 V_2 = P_1' V_2' \text{ at temperature } T_2. \quad (28)$$

If now (27) be subtracted from (28),

$$P_1(V_2 - V_1) = P_1'(V_2' - V_1'); \quad (29)$$

showing the external work to be the same in each case. It is therefore independent of the pressure during the change, provided that pressure is constant and depends only on the value of the initial and final temperatures. It therefore follows that the value of  $C_p$  is independent of the



pressure and is a constant for a perfect gas.

# RELATIONS EXISTING BETWEEN SPECIFIC HEATS.

Returning to equation (25) for a change of temperature of one degree,

$$K_p - K_v = \int_{V_1}^{V_2} P dV,$$

and for any change of temperature

$$K_p(T_2 - T_1) - K_v(T_2 - T_1) = \int_{V_1}^{V_2} P dV, \quad (30)$$

which for constant pressure changes is, by equation (6),

$$K_p(T_2 - T_1) - K_v(T_2 - T_1) = P_1(V_2 - V_1). \quad (31)$$

From equation (18),

$$P_1 V_1 = R_1 T_1 \quad \text{and} \quad P_2 V_2 = R T_2,$$

and when  $P_1 = P_2$ , that is, when the pressure during a change is constant,

$$P_1(V_2 - V_1) = R(T_2 - T_1),$$

so that (31) may be written

$$K_p - K_v = R; \quad (32)$$

showing that  $R$ , the constant in the perfect-gas law, is really the value of the external work done by one pound of gas when undergoing a change of temperature of one degree at constant pressure.

In many cases the ratio of the two specific heats  $\frac{K_p}{K_v}$  occurs, and this is represented by  $\gamma$ . Writing (32)

$$K_v = K_p - R,$$

a useful expression in terms of  $K_v$ ,  $R$ , and  $\gamma$  may be obtained by dividing

by  $K_v$ , substituting  $\gamma$  for  $\frac{K_p}{K_v}$ , and transposing. This gives

$$K_v = \frac{R}{\gamma - 1}. \quad (33)$$

#### TYPE VOLUME CHANGES.

The facts so far developed may now be made use of in deriving the laws governing expansions and compressions of gases. By expansion is meant an increase of volume, and by compression is meant a decrease of volume. There are an infinite number of possible expansions and compressions dependent upon different laws of heat change, but two are of particular importance in the study of heat-engines.

These are called

- (a) Isothermal volume changes, and
- (b) Adiabatic volume changes.

*Isothermal changes are those taking*

*place while the temperature remains constant.*

*Adiabatic changes are those taking place without reception or rejection of heat, as heat, by the body changing volume.*

#### ISOTHERMAL VOLUME CHANGES.

An isothermal change is easily analyzed by means of Boyle's Law, equation (9). If the temperature remains constant,

$$PV = \text{a constant.}$$

Plotting this equation with horizontal distances equal to volumes, and vertical distances equal to pressures, a curve is obtained as shown in Fig. 2. The law of expansion may be regarded as a logarithmic equation of the form

$$PV^n = \text{a constant,}$$

in which  $n$  is equal to unity.

*If external work is done during an isothermal increase of volume, an amount of heat energy equal to the work done must be*

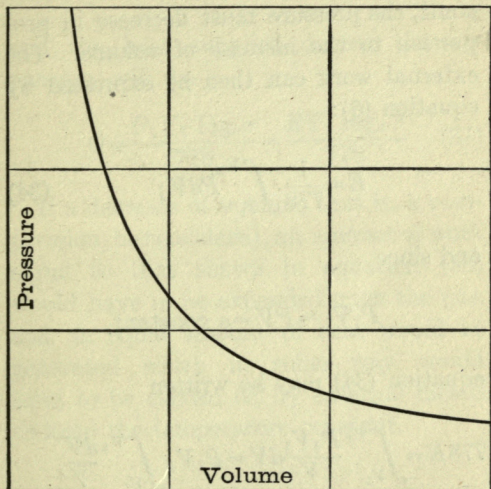


FIG. 2.

*consumed. Since the expanding gas by definition is maintained at constant temperature, the work cannot be done at the expense of its own intrinsic energy. The*



only alternative is that heat equal in amount to external work done be supplied from some outside source. Equation (18) shows that if the temperature of a gas remains constant, the pressure must decrease in proportion to the increase of volume. The external work can then be expressed by equation (6):

$$E = \frac{1}{778} \int_{V_1}^{V_2} P dV; \quad (34)$$

and since

$$P_1 V_1 = PV = \text{a constant},$$

equation (34) may be written

$$778E = \int_{V_1}^{V_2} \frac{P_1 V_1}{V} dV = P_1 V_1 \int_{V_1}^{V_2} \frac{dV}{V},$$

integrating which gives

$$\begin{aligned} 778E &= P_1 V_1 (\log_e V_2 - \log_e V_1) \\ &= P_1 V_1 \left( \log_e \frac{V_2}{V_1} \right). \end{aligned} \quad (35)$$

Calling  $\frac{V_2}{V_1}$  the ratio of expansion,  $r$ ,

$$778E = P_1 V_1 \log_e r = RT_1 \log_e r, \quad (36)$$

and the heat supplied during the expansion will be

$$Q = \frac{P_1 V_1 \log_e r}{778} = \frac{RT_1 \log_e r}{778} \quad (37)$$

If a decrease of volume, that is, a compression, be considered, an amount of work equal to that shown in equation (36) would have to be expended upon the gas, and an equal amount of heat would be generated which in some way would have to be carried off by external means to keep the temperature constant.

#### ADIABATIC VOLUME CHANGES.

*In the case of an Adiabatic Expansion any work done by an increase of volume would have to be done at the expense of heat already contained within the expanding*

gas, because during such an expansion no heat can be received from external sources. That is, the work would be done at the expense of its intrinsic energy and therefore its temperature would drop. Experience has shown that an adiabatic expansion can be represented by the same form of logarithmic equation as that used for the isothermal; in this case, however,  $n$  would have a different value.

$$P_1 V_1^n = P_2 V_2^n = PV^n = \text{a constant} \quad (38)$$

may then be taken as the equation of adiabatic expansion.

The external work would be, as before,

$$778E = \int_{V_1}^{V_2} P dV,$$

and substituting from (38),

$$778E = P_1 V_1^n \int_{V_1}^{V_2} \frac{dV}{V^n},$$

integrating which gives

$$778E = \frac{P_1 V_1^n (V_2^{1-n} - V_1^{1-n})}{1-n}, \quad (39)$$

which by means of equation (38),

$$P_1 V_1^n = P_2 V_2^n,$$

can be written

$$778E = \frac{P_1 V_1 - P_2 V_2}{n-1} = \frac{R(T_1 - T_2)}{n-1}. \quad (40)$$

Since the amount of external work done must be equal to the change of intrinsic energy, and since in a perfect gas this is equal to the change of sensible heat,  $S$ , it follows that

$$K_v(T_1 - T_2) = \frac{R(T_1 - T_2)}{n-1}, \quad (41)$$

and substituting for  $K_v$  by means of (33),

$$\frac{R(T_1 - T_2)}{\gamma - 1} = \frac{R(T_1 - T_2)}{n - 1}, \quad (42)$$

which shows that for adiabatic expansion of a perfect gas

$$n = \gamma,$$

and the equation for such an expansion is

$$P_1 V_1^r = P_2 V_2^r = P V^r = \text{const.} \quad (43)$$

The work being done at the expense of sensible heat, there must be a drop of temperature, and this can be found by combining equation (43) with the law of perfect gases, equation (17). These two give

$$\frac{P_2 V_2^r}{P_1 V_1^r} = 1 \quad \text{and} \quad \frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2},$$

which multiplied together and simplified give

$$\frac{T_1}{T_2} = \left( \frac{V_2}{V_1} \right)^{r-1}; \quad (44)$$

and representing ratio of expansion by  $r$ ,

$$\frac{T_1}{T_2} = r^{r-1}. \quad (45)$$

It is often convenient to have the ratio of the temperatures expressed in terms of the pressures, and this can easily be done by substituting for  $\left( \frac{V_2}{V_1} \right)$  in equa-

tion (44) its value derived from equation (43), giving

$$\frac{T_1}{T_2} = \left( \frac{P_1}{P_2} \right)^{\frac{r-1}{r}}. \quad (46)$$

Adiabatic Compressions are the exact reverse of adiabatic expansions. The work expended by external bodies to compress the gas will all be converted into sensible heat in the gas, since by definition none can be given out by the material under compression. Such being the case, there will be a rise of temperature equal to the drop during expansion between corresponding volume limits. The equations previously developed for external work done by the gas during expansion also give the value of work done upon the gas during compression.

#### AREA AS MEASURE OF EXTERNAL WORK.

It has been shown that both Isothermal and Adiabatic changes may be represented by means of the general equation

$$P_1 V_1^n = P_2 V_2^n = P V^n = \text{a constant},$$



and that the external work in each case can be represented by the equation

$$778E = \int_{V_1}^{V_2} P dV.$$

Such volume changes may be plotted to  $PV$  coordinates and give curves of approximately similar appearance, though with slightly different curvatures and slopes. For the following demonstration the curve of Fig. 3 may be assumed to represent any such volume change.

Since the area  $abcd$  under this curve is

$$A = \int_{V_1}^{V_2} P dV,$$

and since this is the same as the expression for  $E$ ,

$$A = 778E. \quad (47)$$

That is, the area under a curve on a  $PV$  diagram represents external work done by a body expanding according to the law represented by that curve, or represents work done upon a body compressed according to the same law.

In the case of isothermal expansion this area must then equal the heat supplied from external sources during ex-

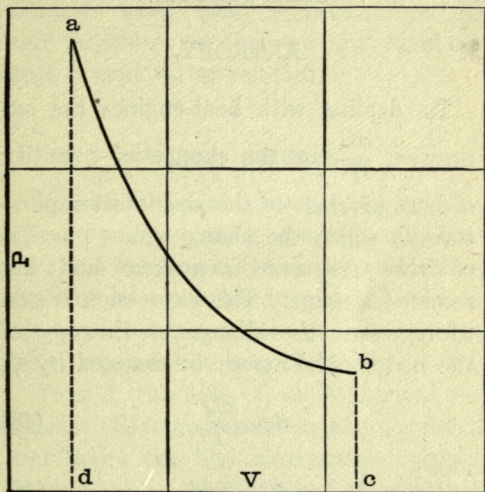


FIG. 3.

pansion, and in the case of adiabatic expansion it must represent the loss of intrinsic energy.

## CHAPTER III.

### ENTROPY.

IN dealing with heat-engines the expression  $\frac{dQ}{T}$ , or the change of quantity of heat divided by the absolute temperature at which the change takes place, is of very frequent occurrence and has received a name. This expression is said to represent the change of Entropy of the body. If Entropy be denoted by  $\phi$ ,

$$d\phi = \frac{dQ}{T}, \quad (48)$$

and

$$dQ = Td\phi, \quad (49)$$

which may be integrated as indicated in the following equation:

$$Q_2 - Q_1 = \int_{\phi_1}^{\phi_2} Td\phi. \quad (50)$$

It can easily be seen from equation (49) above that the entropy of a body must increase when heat is added to it and decrease when heat is taken from it, and therefore remain constant when no heat is received or rejected.

#### ENTROPY DIAGRAMS.

If coordinates be chosen with vertical distances representing absolute temperature and horizontal distances representing entropy, it is possible to plot the various entropy changes which bodies undergo when subjected to heat treatment.

Thus in the case of an isothermal expansion the temperature remains constant, and hence the line representing such a change upon the entropy-temperature diagram must be horizontal as in Fig. 4. Heat having been added to the body at constant temperature, the entropy has increased.

During an adiabatic expansion no heat is received or rejected, and therefore the

entropy must remain constant, that is, the line representing such change must be vertical as in Fig. 4. This shows a drop

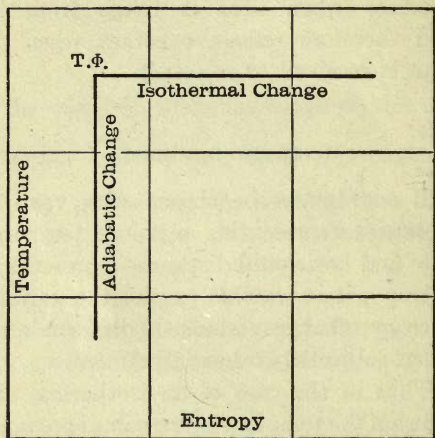


FIG. 4.

in temperature such as actually occurs during adiabatic expansion, or a rise in temperature for adiabatic compression.

## ENTROPY CHANGES.

In the case of Isothermal Expansion, equation (50),

$$Q_2 - Q_1 = \int_{\phi_1}^{\phi_2} T d\phi,$$

becomes

$$Q_2 - Q_1 = T(\phi_2 - \phi_1), \quad (51)$$

since the temperature is constant.

In the case of Adiabatic Expansion, no heat being received or rejected,

$$Q_2 - Q_1 = \int_{\phi_1}^{\phi_2} T d\phi = 0,$$

and therefore

$$d\phi = 0. \quad (52)$$

Thus *the area under a line on the  $T\phi$  diagram represents the heat change; area under a line traced from left to right represents heat supplied to the body, and under a line traced from right to left, heat rejected by the body.*



In a general case of heat change of any kind, equation (48),

$$d\phi = \frac{dQ}{T},$$

may be written

$$d\phi = \frac{CdT}{T},$$

where  $C$  represents the proper specific heat for the conditions governing the heat change. If  $C$  be assumed constant, integration gives

$$\begin{aligned}\phi_2 - \phi_1 &= C \int_{T_1}^{T_2} \frac{dT}{T} = C(\log_e T_2 - \log_e T_1) \\ &= C \log_e \frac{T_2}{T_1},\end{aligned}\quad (53)$$

so that the total change of entropy for a given temperature change can be calculated whenever the proper value of the specific heat is known.

The change of entropy of a perfect gas

when being heated or expanded under constant pressure is then

$$\phi_2 - \phi_1 = C_p \log_e \frac{T_2}{T_1}, \quad (54)$$

and when being heated at constant volume

$$\phi_2 - \phi_1 = C_v \log_e \frac{T_2}{T_1}. \quad (55)$$

## CHAPTER IV.

### CYCLES.

THE working substances of heat-engines are generally in theory carried through some sort of a series of changes in such a way that they periodically return to a certain set of initial or starting conditions. Such a series of changes form what is known as a thermodynamic cycle.

The most interesting of these, both historically and thermodynamically, is the so-called "Cycle of Carnot," or simply "Carnot Cycle." It could be carried out with any material for working substance, but will be investigated here for the case of a perfect gas only.

## THE CARNOT CYCLE.

For the generation of the Carnot cycle several more or less ideal pieces of apparatus are necessary:

1. A cylinder and frictionless piston made of a material which is a perfect non-conductor of heat.
2. A perfectly conducting end or cover for that cylinder and another cover of non-conducting material which may be made to fit over the first.
3. A hot body so arranged as to maintain a constant temperature,  $T_1$ , no matter how much heat be taken from or added to it.
4. A cold body arranged to maintain a constant temperature,  $T_2$ .
5. A working substance enclosed within the cylinder.

Assuming one pound of perfect gas for simplicity, imagine it enclosed within the cylinder between head and piston and having volume and pressure as shown at  $a$  in Fig. 5. Assume its temperature equal to  $T_1$ .

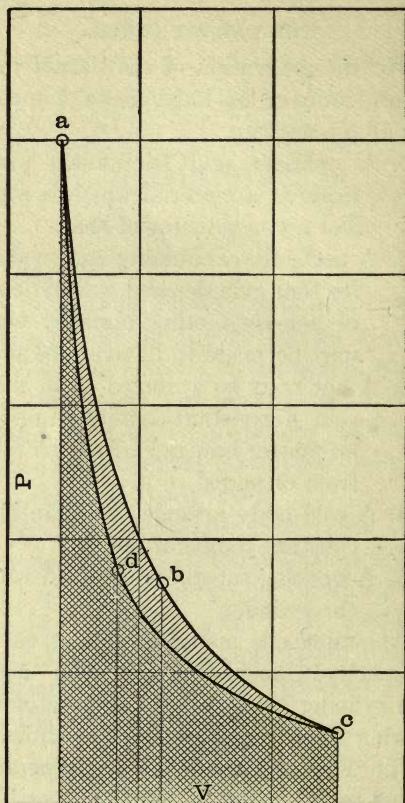


FIG. 5.

Then if the hot body at temperature  $T_1$  be brought in contact with the perfectly conducting cylinder end, the gas may be allowed to expand isothermally, driving out the piston, and receiving any heat necessary from the hot body at a temperature  $T_1$ . Assume this expansion to continue from  $V_a P_a$  conditions to  $V_b P_b$  conditions, and then the hot body to be removed and the cylinder end protected by the non-conducting cover. If expansion continues under these conditions, the body is insulated from heat transfer and therefore the change will be adiabatic. Assume the expansion to continue to  $V_c P_c$  conditions, at which point the temperature has dropped to  $T_2$ , the temperature of the cold body. If now the protecting cover be removed, the cold body be brought in contact with the cylinder, and the piston forcibly driven in, the resulting compression would be isothermal at a temperature  $T_2$ . The heat generated by that compression would be absorbed by the cold body at the low temperature  $T_2$ .



Imagine this compression stopped at a properly chosen point,  $d$ , so that adiabatic compression from that point would bring the body back to initial conditions  $P_aV_a$ . At the time conditions  $P_aV_a$  are arrived at, remove the cold body, replace the protecting cover, and then continue the compression until the  $P_aV_a$  conditions are again attained. The temperature would rise because of the work done upon the gas during compression, and when  $P_aV_a$  conditions were reached the gas would have to have the same temperature as it had to start with, namely,  $T_1$ . Therefore the cycle would be complete.

Since the areas as cross-hatched under curves  $ab$  and  $bc$  would represent external work done by the gas, and the areas under  $cd$  and  $da$  work done upon the gas, the net result of the operation would be the work represented by the area  $abcd$  or that enclosed by the four lines of the cycle.

If efficiency be defined as

$$\begin{aligned}\text{Eff.} &= \frac{\text{Useful result}}{\text{Expenditure made to obtain that result}} \\ &= \frac{\text{Result}}{\text{Effort}},\end{aligned}\quad (56)$$

the efficiency in this case would be

$$\begin{aligned}\text{Eff.} &= \frac{\text{Useful external work}}{\text{Heat suppl'd from hot body to do that work}} \\ &= \frac{\text{Area } abcd \text{ in foot-pounds}}{\text{Heat from hot body in foot-pounds}}.\end{aligned}$$

Since the total amount of energy made available in mechanical form must equal the amount of heat energy which has disappeared, the expression for efficiency may be still further simplified as

$$\begin{aligned}\text{Eff.} &= \frac{\text{Heat supplied} - \text{Heat rejected}}{\text{Heat supplied}} \\ &= \frac{Q_1 - Q_2}{Q_1}.\end{aligned}\quad (57)$$

It is evident that in the expression for efficiency the heat which is rejected cannot be credited to the engine because its temperature is so low that it cannot again be used in that engine.

The operations taking place during this cycle may be analyzed by means of the equations already developed for gases, and the results may be tabulated as below:

Line.	Heat received.	Work done.
<i>ab</i>	$+RT_1 \log_e r$	$+RT_1 \log_e r$
<i>bc</i>	0	$+\frac{R(T_1 - T_2)}{n-1}$
<i>cd</i>	$-RT_2 \log_e r'$	$-RT_2 \log_e r'$
<i>da</i>	0	$-\frac{R(T_1 - T_2)}{n-1}$

The value of  $r'$  in this table can be shown equal to  $r$  as follows:

The drop of temperature during the adiabatic expansion is given by

$$\frac{T_1}{T_2} = \left( \frac{V_c}{V_b} \right)^{\gamma-1},$$

and the rise of temperature during the adiabatic compression is given by

$$\frac{T_1}{T_2} = \left( \frac{V_d}{V_a} \right)^{\gamma-1},$$

so that

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}$$

and

$$\frac{V_b}{V_a} = \frac{V_c}{V_d},$$

giving

$$r = r'.$$

Writing efficiency

$$\text{Eff.} = \frac{\text{Net external work}}{\text{Heat supplied}},$$

the tabulated values give

$$\begin{aligned} \text{Eff.} &= \frac{RT_1 \log_e r - RT_2 \log_e r}{RT_1 \log_e r} \\ &= \frac{T_1 - T_2}{T_1}. \end{aligned} \quad (58)$$

*This result, which is dependent upon temperatures only, is known as the Carnot Efficiency. It is interesting to note that the efficiency of transformation of heat into mechanical energy increases as the*

temperature difference increases, and can never equal unity or 100% unless  $T_2$  is equal to absolute zero.

As will be shown in the succeeding paragraphs, no heat-engine can be constructed which is more efficient than the Carnot, and hence no engine can be expected to have even a theoretical efficiency of 100% under ordinary circumstances.

#### REVERSED HEAT-ENGINES.

There is no reason why the Carnot cycle as just studied could not be carried through in the reverse direction. That is, starting at  $a$ , allow adiabatic expansion to  $d$ , then isothermal expansion in contact with cold body at temperature  $T_2$  until the point  $c$  is reached, then compress adiabatically to  $b$  and then isothermally to  $a$ . The results of such a series of operations would be just the reverse of those in the first case. When carried through in a clockwise direction the cycle

resulted in the removal of a quantity of heat,  $Q_1$ , from the hot body, the doing of a certain amount of external work,  $E$ , and the rejection to the cold body of a certain amount of heat,  $Q_2$ , equal to  $Q_1 - E$ . *When reversed the same amount of heat,  $Q_2$ , would be absorbed from the cold body, the same amount of work,  $E$ , would be received from outside sources, and the sum of the two,  $Q$ , would be given to the hot body.* In this form the apparatus may be considered a heat-pump, since it carries heat from a lower to a higher temperature.

The full extent of the meaning of the term "reversible" should be understood. In the sense in which the word is used here, *no process is reversible unless at its completion it can be immediately carried through in the opposite direction with no change of apparatus.* Thus in the Carnot method of applying heat along an isothermal or at constant temperature, the process is reversible because the heat could again be rejected with all changes



exactly opposite to those during reception by a simple reversal of the direction of motion of the piston. As an example of a non-reversible process, imagine the heating of a gas by bringing it into contact with a body at a higher temperature. No method of doing this can be imagined by a reversal of which the heat can be again extracted from the gas and given back to the source of supply while that gas is in contact with the high-temperature body; that is, no method which will result in leaving the body at the initial high temperature and the gas at the initial low temperature, and which will not involve the use of additional apparatus. An example of a non-reversible process in actual practice is the heating of the working fluid in an internal-combustion engine by the chemical process of combustion.

An engine, then, which is reversible in this thermodynamic way, when run as a pump absorbs the same amount of work as it previously made available, takes

from the cold body the same amount as it previously rejected to it, and gives to the hot body the same amount as it previously absorbed from it. It is a simple matter to prove that such a reversible engine has the maximum possible theoretical efficiency.

For this purpose imagine a reversible engine and another engine of any kind which is assumed to be capable of developing exactly the same amount of useful or external work, but is more efficient, that is, absorbs less heat from the hot body for the purpose of developing that work. Since both engines are equally powerful, either one can drive the other, and it may therefore be assumed that the more efficient may be made to drive the reversible engine as a heat-pump, removing an amount of heat,  $Q_2$ , from the cold body and giving an amount of heat,  $Q_1$ , to the hot body. But since the driving engine which is developing the external work which the pump is absorbing is more efficient than

the pump, it is removing from the hot body an amount of heat,  $Q_1'$ , less than  $Q_1$ , and rejecting to the cold body an amount of heat,  $Q_2'$ , less than  $Q_2$ .

The result of assuming the driving engine more efficient than the driven is to develop a system which, without the reception of any energy from outside sources, is capable of conveying more heat from a low to a high temperature than it carries from the high to the low temperature in keeping itself in operation. This action is contrary to common experience as expressed in the Second Law of Thermodynamics, and is regarded as an absurdity. Therefore the driving engine cannot have an efficiency greater than that of the reversible engine; the best that it can do is to have an equal efficiency. Since the driving engine was not specified as to type, the proof is absolutely general, depends only on common experience as stated in the Second Law, and shows the reversible engine to have as high an efficiency as is attainable.

It is only one step farther to show that all engines, reversible in the same way as the Carnot engine is reversible, must have the same efficiency when operating between the same temperature limits no matter what their cycle of operations. If this were not so, the more efficient could be made to drive the less efficient, giving the absurdity described above.

The Carnot efficiency  $\frac{T_1 - T_2}{T_1}$  is then the maximum possible theoretical efficiency which may be obtained with heat-engines. For this reason it is often used as a standard with which to compare the performances of actual engines.

#### CARNOT CYCLE ON $T\phi$ DIAGRAM.

The shape of the Carnot cycle when drawn on the  $T\phi$  diagram must be as shown in Fig. 6, because the lines  $ab$  and  $cd$  are lines of constant temperature, and the lines  $bc$  and  $ad$  are adiabatics, that is, lines of constant entropy.

Equation (51), which applies to this case, gives

$$Q = T_1(\phi_2 - \phi_1) \quad \text{and} \quad Q_2 = T_2(\phi_2 - \phi_1),$$

so that the efficiency becomes

$$\begin{aligned} \text{Eff.} &= \frac{Q_1 - Q_2}{Q_1} = \frac{T_1(\phi_2 - \phi_1) - T_2(\phi_2 - \phi_1)}{T_1(\phi_2 - \phi_1)} \\ &= \frac{T_1 - T_2}{T_1} \text{ as before.} \end{aligned} \quad (59)$$

Since the area under  $ab$  represents heat received from the hot body and the area under  $cd$  represents heat rejected to the cold body, the area  $abcd$ , which is the difference between them, must equal the heat converted into external work.

It can readily be seen from the diagram of Fig. 6 and the following demonstration that the criterion of maximum efficiency is the reception at the highest temperature of all the heat received from the hot body and the rejection at lowest temperature of all heat rejected to the cold body. If the heat is received at temperatures varying between  $T_d'$  and  $T_1$ , the line

showing entropy change will be given by equation (53) and will have a shape approximately that shown by dotted line  $d'a'$  of Fig. 6. This would result in the

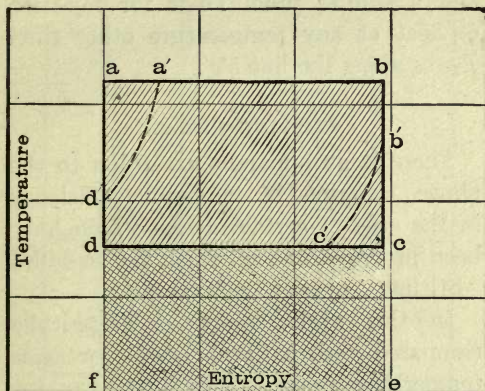


FIG 6

loss of area  $d'aa'$ , which is a much larger proportion of area  $abcd$  than it is of area  $abef$ , and therefore the efficiency, which will now be

$$\text{Eff.} = \frac{a'bcdd'}{a'befd'}$$



will be less than the previous efficiency, which was

$$\text{Eff.} = \frac{abcd}{abef},$$

and a similar proof holds for rejection of heat at any temperature other than  $T_2$ , as along the line  $b'c'$ .

#### STIRLING CYCLE.

There is an apparent exception to the above criterion of maximum efficiency in the case of certain cycles which have been proposed and of which the so-called "Stirling" cycle is an example.

In this cycle, which is graphically compared with a Carnot cycle for same temperature range in Fig. 7, the working substance is expanded isothermally with reception of heat from the body at temperature  $T_1$ , until reaching point  $b$ , when some of its heat is transferred to a device known as a regenerator. The apparatus is so arranged that the pressure drops with the temperature at just the rate necessary to keep the volume constant.

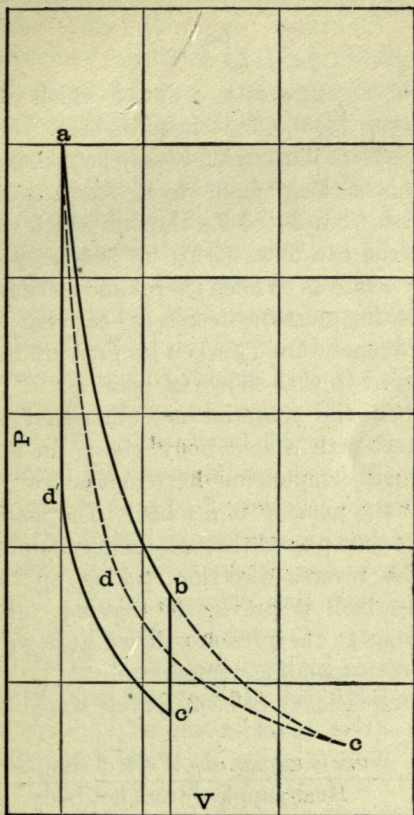


FIG. 7.

The regenerator is a device which can receive, store, and restore heat. For purposes of illustration it may be assumed to be a long pipe, with temperature graded from  $T_1$  to  $T_2$ , through which the material can flow, giving up heat at just such a rate as to keep its volume constant while its pressure decreases, arriving at the temperature  $T_2$  when its pressure has dropped to that shown at point  $c'$ .

Then the material is compressed in contact with a cold body, giving an isothermal compression at temperature  $T_2$  until the point  $d'$  is reached. The material is then passed through the regenerator in the reverse direction, taking up the heat which it previously rejected, until arriving at the pressure shown at  $a$  with the corresponding temperature  $T_1$ .

The efficiency of such a cycle would be

$$\begin{aligned} \text{Eff.} &= \frac{\text{Work of expan. } ab - \text{Work of comp. } c'd'}{\text{Heat supplied from hot body}} \\ &= \frac{RT_1 \log_e r - RT_2 \log_e r}{RT_1 \log_e r} = \frac{T_1 - T_2}{T_1}, \quad (60) \end{aligned}$$

which is seen to be the same as the Carnot cycle. This does not contradict the criterion of maximum efficiency previously arrived at, because, although the body receives heat at varying temperatures along the line  $d'a$  and rejects it similarly along the line  $bc'$ , all the heat received into the system from the hot body is received at the highest temperature, and all that rejected from the system to the cold body is rejected at the lower temperature.

The  $T\phi$  diagram for such a cycle is shown in Fig. 8, where it is the figure  $abc'd'$  superimposed upon the Carnot cycle  $abcd$ . The lines  $d'a$  and  $c'b$  are obtained by means of equation (55) and are readily seen to be parallel curves, so that the areas  $d'ad$  and  $c'bc$  are equal and therefore the areas  $abc'd'$  and  $abcd$  are equal. The efficiency in each case is the area of the cycle divided by the area  $abef$ , which is the heat received along the line  $ab$ , and therefore the two efficiencies are equal. The heat received by the hot body along  $d'a$  and rejected along the

line  $bc'$  never really leaves the system or apparatus and may be considered as simply short-circuited during part of the cycle.

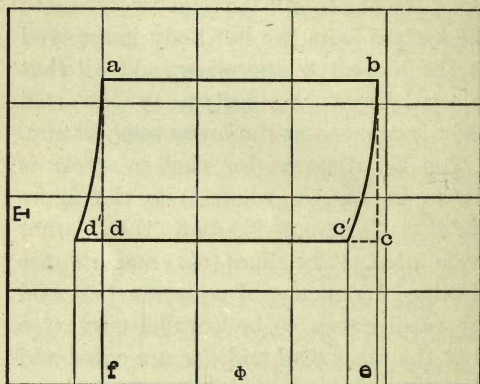


FIG. 8.

### OTTO CYCLE.

Another cycle of interest is the "Otto" cycle, which is the theoretical cycle of most of the gas-engines built at the present time. Drawn on the  $PV$  diagram, it has the shape shown in Fig. 9. Heat is added

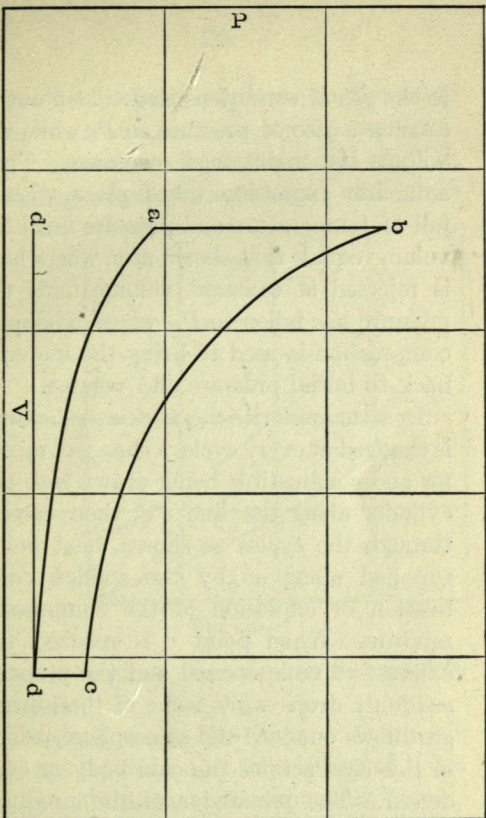


FIG. 9.



to the gas at conditions shown at point  $a$ , causing a rise of pressure to  $P_b$  while the volume is maintained constant. Then adiabatic expansion takes place with a fall of temperature and pressure until the volume equals that shown at  $c$ , where heat is rejected at constant volume until the pressure has fallen to  $P_d$ , where adiabatic compression is used to bring the material back to initial pressure and volume.

In actual practice the working substance is changed at every cycle, a charge of mixed air and combustible being drawn into the cylinder along the line  $d'd$ , then carried through the cycles as shown, heat being supplied along  $ab$  by the sudden combustion or explosion of the compressed mixture. When point  $c$  is reached the exhaust-valve is opened and the pressure suddenly drops while some of the burned gas blows out into the atmosphere, which in this case acts as the cold body or condenser. The remainder of the products of combustion is exhausted along the line  $dd'$ . Thus while in the theoretical

case the working substance is the same time after time, and two strokes are necessary for each cycle, in the actual case the working substance is changed each cycle

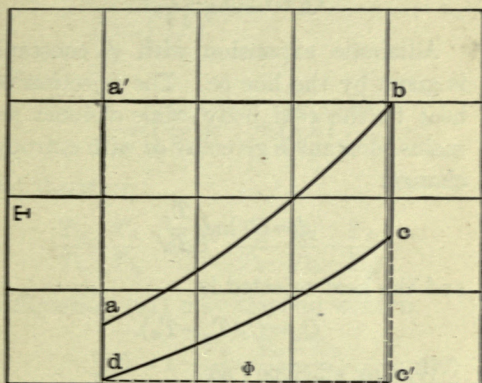


FIG. 10.

and it requires four strokes to complete a cycle.

Fig. 10 shows the shape of this cycle on the  $T\phi$  diagram. The letters of Figs. 9 and 10 designate corresponding points.

The line  $ab$  in the  $T\phi$  diagram represents the addition of heat at constant

volume, and the change of entropy is given by

$$\phi = C_v \log_e \frac{T_b}{T_a};$$

the heat added is

$$Q_1 = C_v(T_b - T_a).$$

Adiabatic expansion with  $\phi$  constant is given by the line  $bc$ . The rejection of heat to the cold body while volume remains constant is given by  $cd$  with entropy change:

$$\phi = C_v \log_e \frac{T_c}{T_d},$$

and the heat rejected is

$$Q_2 = C_v(T_c - T_d).$$

Writing efficiency as

$$\text{Eff.} = \frac{Q_1 - Q_2}{Q_1},$$

$$\begin{aligned} \text{Eff.} &= \frac{C_v(T_b - T_a) - C_v(T_c - T_d)}{C_v(T_b - T_a)} \\ &= 1 - \frac{T_c - T_d}{T_b - T_a}. \end{aligned} \quad (61)$$

Since the curves  $bc$  and  $da$  represent adiabatic changes, the ratio of the various temperatures may be expressed by means of equation (44) as

$$\frac{T_c}{T_b} = \left( \frac{V_b}{V_c} \right)^{\gamma-1}$$

and

$$\frac{T_d}{T_a} = \left( \frac{V_a}{V_d} \right)^{\gamma-1} = \left( \frac{V_b}{V_c} \right)^{\gamma-1},$$

and therefore

$$\frac{T_c}{T_b} = \frac{T_d}{T_a} \quad \text{and} \quad \frac{T_c - T_d}{T_b - T_a} = \frac{T_d}{T_a}.$$

Equation (61) may then be written

$$\text{Eff.} = 1 - \frac{T_d}{T_a} = \frac{T_a - T_d}{T_a}, \quad (62)$$

or

$$\text{Eff.} = 1 - \left( \frac{V_a}{V_d} \right)^{\gamma-1}; \quad (63)$$

showing the rather curious fact that the efficiency of this cycle theoretically depends only upon the temperature ratio or volume ratio of the adiabatic compression.

This cycle can be graphically compared with the Carnot cycle for same temperature limits by means of the diagram  $a'bc'd$ , and the efficiency for the Otto cycle can be shown to be less than that of the Carnot by a discussion similar to that given for the dotted-line cycle of Fig. 6.

#### REFRIGERATING-MACHINES.

Refrigerating-machines using gases for a working substance are still used to a certain extent, and therefore their cycles should be considered here. In the discussion of the Carnot engine it was shown that when reversed it acted as a heat-pump, removing heat from the body at a low temperature and rejecting it to a body at a high temperature. Thus a heat-pump is nothing but what is ordinarily known as a refrigerating-machine.

Any reversible cycle could be used for refrigerating-machinery, though all reversible gas-cycles are very inconvenient for practical application. Several cycles



which are not thermodynamically reversible may in a different sense be carried through in the reverse direction by properly constructed mechanism. That is, apparatus can be devised which when operated gives a cycle traced in the counter-clockwise direction similar to that traced in a clockwise direction by an engine.

#### THE JOULE CYCLE.

The Joule cycle is a very good example of such conditions. It has the shape shown in Fig. 11, when drawn to  $PV$  coordinates. The operation when the cycle is traced by an engine is as follows: Gas with pressure and volume as shown at  $a$  is compressed adiabatically to conditions at  $b$ ; it is then brought in contact with a hot body at temperature equal to  $T_1$ , greater than that of the gas at  $b$ . Heat is received and pressure maintained constant while temperature and volume increase until conditions are as shown at  $c$ . The temperature of the gas,  $T_c$ ,



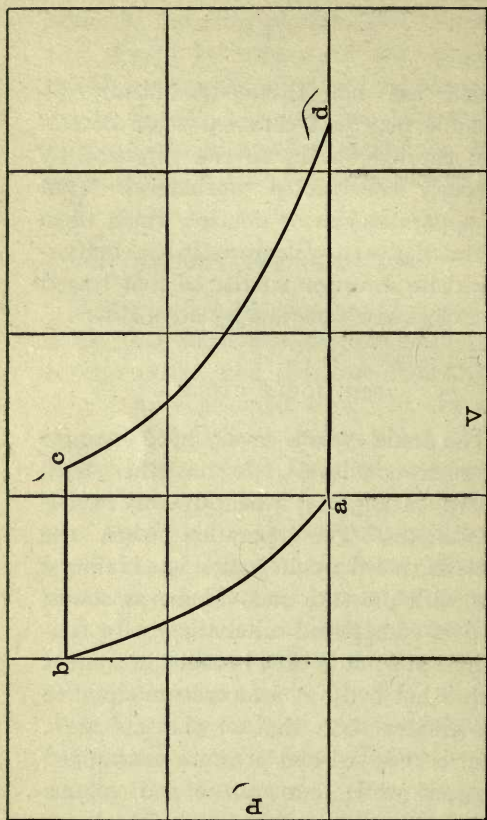


FIG. 11.

may or may not be as great as  $T_1$ ; it cannot be greater. Adiabatic expansion brings the body to conditions  $V_a$  and  $P_a$ , and then the heat is rejected to a body at low temperature,  $T_2$ , while the volume and temperature decrease with constant pressure. The temperature  $T_2$  must be at least as low as  $T_a$ , and may be lower.

To make this device act as a heat-pump the gas must expand at constant pressure from  $V_a$  to  $V_d$ , while the temperature rises, due to the absorption of heat from the cold body. That body must now have a temperature at least as high as  $T_d$ , showing immediately that this cycle is not thermodynamically reversible, because a change of apparatus is necessary for reversal. The line from  $d$  to  $c$  represents adiabatic compression, and at  $c$  the gas begins to reject heat to the hot body, which now must have a temperature no higher than that of the gas when at  $V_bP_b$ . The rejection of heat continues until point  $b$  is reached, when the gas is expanded

adiabatically to  $a$  and the cycle is complete.

The performance of the cycle has resulted in removing an amount of heat,  $Q_2$ , from the cold body, and the giving to the hot body of an amount,  $Q_1$ , equal to  $Q_2$  plus the work of compression from  $d$  to  $c$ .

The cycle as drawn to  $T\phi$  coordinates is shown in Fig. 12 where all the letters correspond to those in Fig. 11. The heat removed from the cold body is given by the area  $eadf$ , which represents the amount of heat received by the gas at constant pressure and is equal to

$$Q_2 = C_p(T_a - T_d).$$

The heat added to the hot body is similarly the area  $ebcf$ , and equals

$$Q_1 = C_p(T_c - T_b).$$

The useful result in this cycle is the amount of heat removed from the cold body, and the expenditure of energy is the amount received from external sources

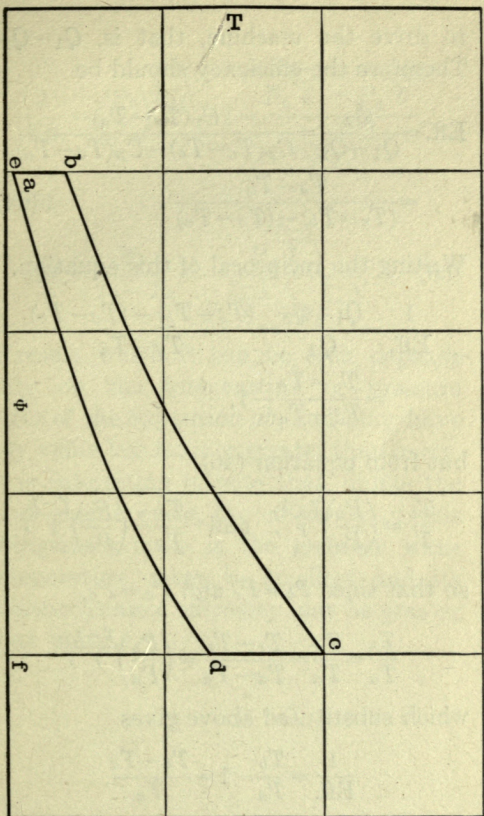


FIG. 12.

to drive the machine, that is,  $Q_1 - Q_2$ . Therefore the efficiency should be

$$\begin{aligned} \text{Eff.} &= \frac{Q_2}{Q_1 - Q_2} = \frac{C_p(T_d - T_a)}{C_p(T_c - T_b) - C_p(T_d - T_a)} \\ &= \frac{T_d - T_a}{(T_c - T_b) - (T_d - T_a)} \end{aligned} \quad (64)$$

Writing the reciprocal of this equation,

$$\begin{aligned} \frac{1}{\text{Eff.}} &= \frac{Q_1 - Q_2}{Q_2} = \frac{(T_c - T_b) - (T_d - T_a)}{T_d - T_a} \\ &= \frac{T_c - T_b}{T_d - T_a} - 1, \end{aligned}$$

but from equation (46)

$$\frac{T_b}{T_a} = \left(\frac{P_b}{P_a}\right)^{\frac{\gamma-1}{\gamma}}, \quad \text{and} \quad \frac{T_c}{T_d} = \left(\frac{P_c}{P_d}\right)^{\frac{\gamma-1}{\gamma}},$$

so that since  $P_b = P_c$  and  $P_a = P_d$ ,

$$\frac{T_b}{T_a} = \frac{T_c}{T_d} = \frac{T_c - T_b}{T_d - T_a} = \left(\frac{P_b}{P_a}\right)^{\frac{\gamma-1}{\gamma}},$$

which substituted above gives

$$\frac{1}{\text{Eff.}} = \frac{T_b}{T_a} - 1 = \frac{T_b - T_a}{T_a},$$

or

$$\frac{1}{\text{Eff.}} = \left(\frac{P_b}{P_a}\right)^{\frac{r-1}{r}} - 1 = \frac{P_b^{\frac{r-1}{r}} - P_a^{\frac{r-1}{r}}}{P_a^{\frac{r-1}{r}}},$$

giving

$$\text{Eff.} = \frac{T_a}{T_b - T_a} = \frac{P_a^{\frac{r-1}{r}}}{P_b^{\frac{r-1}{r}} - P_a^{\frac{r-1}{r}}}, \quad (65)$$

a result which it can be seen depends only on the temperature or pressure ratio of the expansion  $ab$ , and may have any value less than or greater than unity. It is interesting to note that, unlike the heat engine cycle, the efficiency of this refrigerator cycle is the greatest when temperature range is smallest and its thermodynamic efficiency may be greater than unity.



## CHAPTER V.

### FLOW OF GASES.

THE flow of gases through pipes and nozzles may be investigated by means of thermodynamic equations slightly modified to fit the conditions. The equations derived vary somewhat as the assumed conditions of flow vary, and as the limits of this small book preclude a lengthy discussion, only the simplest case will be considered.

Assume a very large reservoir which is constantly supplied with gas at a pressure  $P_1$  so that the pressure within the vessel is always maintained at that value. The corresponding temperature is  $T_1$ , and the volume of unit weight is  $V_1$ . Further, assume a short pipe connected into the side of the vessel, as shown in Fig. 13,

in such a way as to give rounded corners at  $a$ , so that the gas may enter it without serious disturbance. If this short pipe or nozzle communicate with a large space

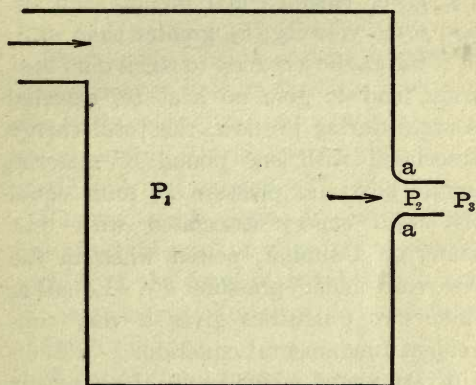


FIG. 13.

in which a constant lower pressure,  $P_3$ , is maintained, there will be a steady flow of gas as indicated by the arrow. In order that this steady flow through the nozzle may be maintained, the gas within the reservoir at some distance from that

opening will have to flow toward it with a constant and definite velocity, which may be designated as  $v_1$ . Within the tube the gas will have some pressure,  $P_2$ , lower than  $P_1$  and higher than  $P_3$ , and some velocity,  $v_2$ , greater than  $v_1$ .

If the gas be assumed to receive no heat from, and to give no heat to, external sources during its flow, the total energy associated with one pound of material in the nozzle at pressure  $P_2$  must equal the total energy associated with that same, or a similar, pound when in the reservoir under pressure  $P_1$ . Equating these two quantities gives a very convenient fundamental equation.

Every pound which leaves the reservoir under the pressure  $P_1$  must be forced out of that reservoir, and therefore external work equal to  $P_1 V_1$  must be done upon it just as though it were being forced out by a piston which swept through the volume  $V_1$  under the pressure  $P_1$  in discharging one pound of gas.

Similarly, every pound of gas flowing

in the nozzle under pressure  $P_2$  displaces its own volume against the constant pressure  $P_2$  and does an amount of work  $P_2V_2$ , just as if it drove a piston through the volume  $V_2$  under the constant pressure  $P_2$ .

Every pound has a certain amount of kinetic energy when in the large reservoir, due to its velocity  $v_1$ , and a certain different amount of kinetic energy when in the small tube and moving with velocity  $v_2$ .

Further, every pound in the reservoir has a certain amount of energy associated with it in the form of sensible heat, and the same is true of every pound as it flows through the tube.

Equating total energy associated with one pound in the reservoir to total energy associated with one pound in the tube gives

$$P_1V_1 + \frac{v_1^2}{2g} + JS_1 = P_2V_2 + \frac{v_2^2}{2g} + JS_2, \quad (66)$$

so that

$$\frac{v_2^2}{2g} - \frac{v_1^2}{2g} = P_1V_1 - P_2V_2 + J(S_1 - S_2). \quad (67)$$

Since the difference in sensible heat is equal to the real specific heat into the difference of temperatures,

$$J(S_1 - S_2) = K_v(T_1 - T_2) = K_v T_1 - K_v T_2,$$

and

$$\frac{v_2^2}{2g} - \frac{v^2}{2g} = P_1 V_1 - P_2 V_2 + K_v T_1 - K_v T_2.$$

The velocity in the reservoir may be neglected as very small, so that

$$\frac{v_2^2}{2g} = P_1 V_1 - P_2 V_2 + K_v T_1 - K_v T_2.$$

Substituting from the law of perfect gases and then factoring gives

$$\begin{aligned} \frac{v_2^2}{2g} &= P_1 V_1 - P_2 V_2 + K_v \frac{P_1 V_1}{R} - K_v \frac{P_2 V_2}{R} \\ &= \left(1 + \frac{K_v}{R}\right) (P_1 V_1 - P_2 V_2), \end{aligned}$$

and since

$$K_v = \frac{R}{\gamma - 1},$$

it follows that

$$\frac{v_2^2}{2g} = \frac{\gamma}{\gamma-1} (P_1 V_1 - P_2 V_2),$$

and

$$v_2 = \sqrt{2g \frac{\gamma}{\gamma-1} (P_1 V_1 - P_2 V_2)}. \quad (68)$$

The weight in pounds per second,  $W$ , can be found if the sectional area,  $a$ , of the tube is known. Since

$$W = \frac{v_2 a}{V_2},$$

the discharge per second is

$$W = \frac{a}{V_2} \sqrt{2g \frac{\gamma}{\gamma-1} (P_1 V_1 - P_2 V_2)}.$$

With the assumption, made above, of no heat-energy transfer to or from external sources during the flow, the drop in pressure from  $P_1$  to  $P_2$  must be an adiabatic expansion, and

$$P_2 V_2^\gamma = P_1 V_1^\gamma,$$



so that

$$P_2 V_2 = P_1 V_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1},$$

and

$$P_2 V_2 = P_1 V_1 \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}.$$

Substituting for  $P_2 V_2$  in (68) gives

$$v_2 = \sqrt{2gP_1 V_1 \frac{\gamma}{\gamma-1} \left\{ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right\}}, \quad (69)$$

and then

$$W = \frac{a}{V_2} \sqrt{2gP_1 V_1 \frac{\gamma}{\gamma-1} \left\{ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right\}}.$$

Since

$$V_2 = V_1 \left( \frac{P_1}{P_2} \right)^{\frac{1}{\gamma}},$$

it follows that

$$W = \frac{a}{V_1 \left( \frac{P_1}{P_2} \right)^{\frac{1}{\gamma}}} \sqrt{2gP_1 V_1 \frac{\gamma}{\gamma-1} \left\{ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right\}}. \quad (70)$$

These equations give the velocity of flow and the quantity discharged when

the initial conditions and the tube pressure,  $P_2$ , are known. In most problems of this character  $P_3$ , the second reservoir pressure, is known, but  $P_2$  is unknown and must be calculated. Unfortunately  $P_2$  bears no simple relation to  $P_3$ , and the ratio between the two must be experimentally determined.

Experiments with air show that  $P_2$  decreases according to a rather complicated expression as  $P_3$  decreases, until  $P_3$  has arrived at a value equal to  $\frac{P_1}{2}$ , when the value of  $P_2$  is approximately equal to  $0.58P_1$ . Further decrease in the value of  $P_3$  causes no diminution in the discharge-tube pressure. Thus the maximum discharge will take place when  $P_3$  is equal to or less than  $\frac{P_1}{2}$ .

It is interesting to note that a mathematical determination of the pressure  $P_2$  for maximum discharge can be found by means of equation (70), and shows that maximum to occur when  $P_2$  is approxi-

mately equal to  $0.53P_1$ . Thus the theoretical and experimental values apparently do not check, but as yet the experimental data are rather meagre, so that the figure given may not be final. It should also be remembered that the equations for flow are determined for ideal conditions and for perfect gases, while experiments must be made with actual apparatus and with real imperfect gases.

## CHAPTER VI.

### VAPORS.

IN the chapter on gases it was noted that the laws developed for the ideal "Perfect Gas" are very approximately true for the real gases when far removed from their points of liquefaction. The nearer real gases are brought to the temperatures and pressures at which liquefaction occurs, the farther do they deviate from these laws. Substances are called vapors when between the conditions under which they may be treated as perfect gases and those under which they exist as liquids.

#### TEMPERATURE OF VAPORIZATION.

Obviously there is no fixed point at which a substance ceases to be a vapor

and becomes a practically perfect gas, the allowable amount of variation from perfect gas laws being simply a matter of personal taste or convenience. There is, however, under any given conditions, a very definite and fixed point at which a liquid changes to a vapor or a vapor becomes a liquid. For every pressure there is a temperature for every substance above which that substance cannot exist in the liquid form. *Each of these temperatures is called the temperature of vaporization for the liquid under consideration for each particular pressure.* Thus the temperature of vaporization for water under a pressure of 14.7 lbs. per square inch is  $212^{\circ}$  Fahrenheit.

The temperature of vaporization rises with the pressure according to laws which must be experimentally determined for every individual substance. This fact is what would naturally be expected, because vaporization is always accompanied by an increase of volume, and anything which would tend to prevent this increase would

make necessary a higher temperature for the separation of the molecules. An increase of pressure might be regarded as assisting the internal attractions in preserving the liquid form against the separating and expanding tendencies accompanying the rise of temperature of, or the increase of heat energy associated with, the substance.

#### SATURATED AND SUPERHEATED VAPOR.

*A vapor which is just on the point of liquefaction, so that any increase of pressure or drop of temperature will cause partial or total condensation, is called a saturated vapor.* If it be removed farther from the liquid state by even an infinitesimally small amount, it is called a "Superheated Vapor." Continuing in the same direction, the material becomes finally a practically perfect gas. It is therefore possible to regard a perfect gas simply as a very highly superheated vapor, and to take the extent of superheating as a measure of gaseous perfection.



## PROCESS OF VAPORIZATION.

The laws of vapors are most easily developed by studying the production of vapor from a liquid, and then the gradual development of a more and more nearly perfect gas from that vapor as it is superheated.

Assume for this purpose a non-conducting cylinder with axis vertical and fitted with a frictionless piston. Beneath this piston imagine unit weight of a liquid and assume the piston to have such weight as to exert a pressure of  $P$  pounds per square foot on the surface of the liquid.

If now the liquid be heated, it will rise in temperature with a slight increase of volume, absorbing heat equal to

$$Q = C(T_2 - T_1), \quad (71)$$

where  $T_2$  and  $T_1$  are final and initial temperatures, and  $C$  is the average specific heat for that temperature range.

The temperature will continue to rise

until a value is reached at which, under the existing pressure, vaporization will take place. Further addition of heat will then cause vaporization with an enormous increase of volume but no increase of temperature until all of the liquid has been evaporated. If heat be added after the vaporization is complete, the volume will still further increase and the temperature will rise until the material is finally so far removed from the liquid state as to be a sensibly perfect gas.

If the operation is repeated with a piston of different weight, the same series of events will take place, but the values of temperature, volume, and heat supplied will be different. A piston giving a greater pressure per square foot will cause a higher temperature of vaporization, a smaller volume of resultant saturated vapor, and the absorption of a different quantity of heat during vaporization. A piston giving a pressure less than the first will cause a lower temperature of vaporization, a

larger saturated vapor volume, and a still different heat absorption.

#### HEAT CONTENT OF VAPOR.

It is convenient to consider the heat required for the process of vaporization as divided into three parts:

(1) Heat necessary to raise the temperature of liquid to the temperature of vaporization, which heat is called "Heat of the Liquid" and represented by  $q$  when dealing with unit weight of material.

(2) That necessary to change the liquid at vaporization temperature to a saturated vapor at the same temperature, known as "Latent Heat of Vaporization" and represented by  $r$  when dealing with unit weight.

(3) Heat necessary to superheat or raise the temperature of the vapor above the temperature of saturation, known as "Superheat" and generally expressed in terms of the temperature to which superheating has been carried; that is, a vapor

is spoken of as having a certain number of degrees of superheat, meaning that it has been raised that many above the temperature of vaporization. The degree of superheat is most often represented by  $D$ .

The latent heat of vaporization,  $r$ , is still further divided into two parts:

(a) The Internal Latent Heat of Vaporization, designated by  $\rho$  for unit weight.

(b) The External Latent Heat of Vaporization, designated by the group symbol  $APu$ , when, as before, dealing with unit weight.

The first, (a), represents the heat necessary to do the internal work of separation of molecules when the volume changes from that of a liquid to that of a saturated vapor. The second, (b), represents the heat necessary to do the work of displacing the surrounding or enveloping medium, as the driving out of the piston in the case just considered.

The group of symbols,  $APu$ , is equivalent to the expression already developed

for external work during constant pressure expansion, that is,  $P(V_2 - V_1)$ . Since this expression is in terms of pounds and feet, the result will be foot-pounds of work. To express the same quantity in British Thermal Units (B.T.U.) it must be divided by Joule's Equivalent,  $J = 778$ .

Representing  $\frac{1}{J}$  by  $A$ , and  $(V_2 - V_1)$  by  $u$ , the expression for external work in British Thermal Units becomes

$$E = APu,$$

which is the form used in dealing with liquids and vapors.

To sum up, the quantity of heat per unit of weight which must be added to a liquid to convert it into a more or less perfect gas at a temperature above that of vaporization is

$$Q = \text{Heat of liquid} + \text{Heat of vaporization} \\ + \text{Superheat},$$

which may be represented in symbols by putting

$$q = \text{Heat of liquid} = C_l(T_v - T_1),$$

where  $T_1$  is initial temperature of liquid and  $T_v$  is vaporizing temperature under the existing pressure conditions;

$$r = \text{heat of vaporization} = \rho + APu,$$

and

$$C_v D = C_v(T_s - T_v) = \text{Superheat},$$

where  $C$  is the specific heat of the vapor and  $D$  represents the number of degrees to which the substance is raised above vaporization temperature,

giving

$$Q = q + r + C_v D. \quad (72)$$

If the liquid is converted into saturated vapor but not superheated, a case occurring so frequently that the special symbol  $\lambda$  is used to represent the heat required,

$$Q = q + r = \lambda = q + \rho + APu = S + I + E. \quad (73)$$

If the liquid is only partly vaporized, that is, all raised to the temperature of



vaporization and then only enough heat added to convert  $x/100$  of it to the vaporous form, the expression for heat per pound takes the form

$$Q = q + \frac{x}{100}r = q + \frac{x}{100}\rho + \frac{x}{100}APu. \quad (74)$$

The term  $x$  is called the "quality" and is generally given in per cent. Thus a quality of 75% means a mixture of 0.75 by weight of saturated vapor and 0.25 liquid at the temperature of vaporization. As a matter of custom, the letter  $x$  is used indifferently to represent per cent quality and the fraction  $x/100$  as given above, so that equation (73) is generally written

$$Q = q + xr. \quad (75)$$

This expression will of course give the correct value independent of the state of mixture of liquid and vapor, that is, it makes no difference whether the liquid is all collected at the bottom of a vessel with the vapor above it, or the liquid in the form of small drops is distributed

throughout the entire volume of the vapor. The latter is the condition more often met with in practice.

A mixture of a saturated vapor with its liquid is spoken of as a Wet Vapor, and a saturated vapor existing absolutely free of its liquid is called a Dry Vapor. Thus starting with liquid, the complete list of the various possible forms is

(a) Liquid below temperature of vaporization.

(b) Liquid at temperature of vaporization.

(c) Mixture of liquid and vapor, or wet saturated vapor.

(d) Dry saturated vapor.

(e) Superheated vapor.

(f) Very highly superheated vapor, or practically perfect gas.

Studying the heat content of vapors in accordance with equation (2),

$$Q = S + I + E,$$

the quantity  $q$  may be taken as the sensible heat  $S$  if the small increase of

volume of liquid with temperature rise be neglected; the quantity  $\rho$  may represent the heat of internal work,  $I$ ; the quantity  $APu$  the heat of external work. Thus  $q + \rho$  might be called the intrinsic energy of a dry vapor, and  $q + x\rho$  the intrinsic energy of a wet vapor, both above  $32^{\circ}$  F.

In the case of a superheated vapor the additional heat must be divided into intrinsic energy, or  $S + I$ , and energy of external work,  $E$ . That is, part is used to increase the temperature and to separate the molecules against their mutual attractions, and part to displace the surrounding media. Measuring the last, the sum of the first two can be found by substitution from the total heat of superheat.

#### VAPOR TABLES.

The values of the various quantities of heat required for different purposes during the vaporization processes of various liquids are determined by experi-

ments assisted, or rather completed, by thermodynamic calculations. It is therefore convenient to arrange them in tables, so that they are readily obtainable. Such tables are known as vapor tables, or, taking cognizance of the material to which their values apply, Steam Tables, Ammonia Tables, Carbon-dioxide Tables, etc. In the first two columns of such tables are generally given pressures increasing by convenient increments through the entire experimental range, and the corresponding temperatures of vaporization, that is, the temperature at which vaporization of that particular liquid will occur under each pressure tabulated. Following these are given in separate columns each of the quantities  $q$ ,  $r$ ,  $\rho$ ,  $APu$ ,  $\lambda$ , and then other convenient data, such as specific volume, etc., for each pressure or temperature.

Since

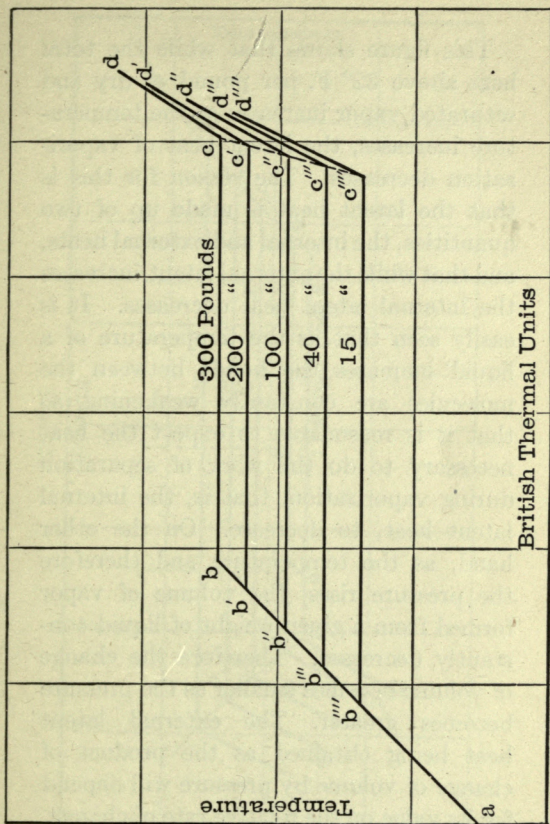
$$q = C_l(T_v - T_1),$$

and only  $T_v$ , the temperature of vapor-

zation, is fixed by the pressure, it is customary to assume the value  $T_1$  at some convenient figure for each liquid. Thus it is common to construct steam tables to give heat of liquid,  $q$ , and total heat,  $\lambda$ , above the temperature of  $32^\circ$  F., that is,  $T_1$  is arbitrarily set at  $32^\circ$  F. For other tables different but equally convenient values of  $T_1$  are chosen.

#### GRAPHIC REPRESENTATION OF VAPORIZATION.

The entire process of vaporization and superheating of water at several pressures is shown graphically by Fig. 14. The specific heat of liquid water has been considered constant for this diagram, so that  $ab$  is a straight line. This line would be curved had the real variable specific heat been used. In studying the figure it should be noticed what a large part of the total heat of the superheated vapor is that absorbed during the process of vaporization.





This figure shows that while the total heat above 32° F. per pound of dry and saturated vapor increases as the temperature increases, the latent heat of vaporization decreases. The reason for this is that the latent heat is made up of two quantities, the internal and external heats, and that while the external latent increases the internal latent heat decreases. It is easily seen that as the temperature of a liquid increases the bonds between the molecules are constantly weakening, so that it is reasonable to expect the heat necessary to do the work of separation during vaporization, that is, the internal latent heat, to decrease. On the other hand, as the temperature and therefore the pressure rises, the volume of vapor formed from a given weight of liquid constantly decreases. Therefore the change of volume becomes smaller as the pressure becomes greater. The external latent heat being obtained as the product of change of volume by pressure will depend for its value on the relative rate of change.

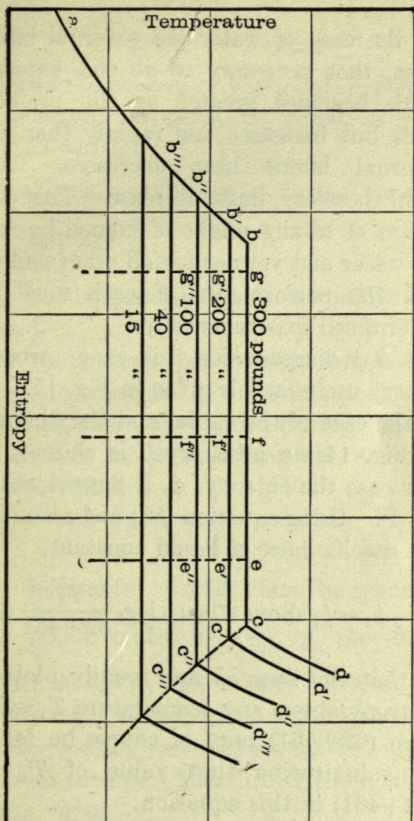


Fig. 15.

In the case of water the external latent heat, that necessary to do this external work, becomes greater as the pressure rises, but increases less rapidly than the internal latent heat decreases. Their sum, therefore, must decrease. This condition of affairs might of course be true for water and yet not for all other vapors, and the performance of each must be determined experimentally.

A  $T\phi$  diagram for this same process is very useful and is given in Fig. 15. As in the case of the tables and the diagram of Fig. 14, an arbitrary 0 is chosen; in this case the entropy,  $\phi$ , is figured above  $32^\circ$  F. Using equation (53) and assuming the specific heat of liquid constant,

$$\phi_2 - \phi_1 = \phi_l \text{ above } 32 = C_l \log_e \frac{T_v}{32 + 461}, \quad (76)$$

so that the lines  $ab$  are readily plotted. Entropy above any temperature  $T_1$  other than  $(32 + 461)$  may of course be found by substituting that value of  $T_1$  for  $(32 + 461)$  in this equation.

## ENTROPY OF VAPOR.

Since the process of vaporization occurs at constant temperature, equation (48) may be written

$$\phi_2 - \phi_1 = \phi_v = \text{change of } \phi \text{ during vaporization} = \frac{r}{T_v}, \quad (77)$$

and the horizontal line  $bc$  is readily obtained.

If the process of vaporization is not complete, that is, if the final quality is less than unity, heat added during vaporization will be  $xr$  and then the entropy change will be

$$\phi_v = \frac{xr}{T_v}. \quad (78)$$

The horizontal would then be shorter and would really be  $\frac{x}{100}$  of the total length of  $bc$ , as can readily be seen by comparing (76) and (77). The length of the line for any case divided by the length  $bc$  must then be a measure of the quality of the vapor.

For the line *cd* representing superheating, the change of entropy can be found by means of equation (53), which rewritten to suit these conditions is

$$\begin{aligned}\phi_2 - \phi_1 = \phi_s &= \text{change during superheating} \\ &= C_p \log_e \frac{T_v + D}{T_v}.\end{aligned}\quad (79)$$

The specific heat of steam vapor at constant pressure is used because the process of vaporization and superheating has been considered under constant pressure conditions. It is of course possible to develop equations for conditions of variable pressure, but it only complicates the problem and gives results which are not required for elementary work.

Summing up, the total entropy of superheated vapor, considered above the arbitrary zero, 32° F., is

$$\begin{aligned}\phi_l + \phi_v + \phi_s &= C_l \log_e \frac{T_v}{32 + 461} + \frac{r}{T_v} \\ &+ C_p \log_e \frac{T_v + D}{T_v},\end{aligned}\quad (80)$$

and when the vapor is wet instead of superheated

$$\phi_l + \phi_v = C_l \log_e \frac{T_v}{32 + 461} + \frac{xr}{T_v}. \quad (81)$$

There is a great difference in the way in which superheated vapors and saturated vapors behave when brought into contact with the liquid form of the same material. Thus, if the saturated vapor of a liquid be brought in contact with that liquid at the same temperature and pressure, there will be no loss of heat by the vapor and it is said to be in thermal equilibrium with its liquid. On the other hand, if the superheated vapor of the same liquid be brought into contact with that liquid at the same pressure and at the temperature of vaporization, the superheat will diminish. That is, heat will be given up by the vapor and will be absorbed by the liquid as heat of vaporization. This process will continue until the superheat has all disappeared, leaving a saturated vapor mixed with



that generated by the absorption of heat by the liquid; or, if the superheat be great enough in quantity, until the liquid is entirely vaporized and the resultant vapor superheated to a temperature equal to that of the vapor giving up heat. A vapor in a superheated condition cannot therefore exist in the presence of its liquid, it being necessary to entirely vaporize any liquid before superheating can begin. This is recognized by saying that a superheated vapor is not in thermal equilibrium with its liquid.

A very useful curve may be obtained by plotting the specific volumes of saturated vapors against the corresponding pressures. This gives what is called the Saturation Curve. It is useful as indicating the volume that unit weight of saturated vapor will have at any given pressure. For steam it is almost perfectly expressed by the equation

$$PV^{\frac{17}{8}} = \text{constant} \quad (82)$$

through the common temperature ranges.

## EVAPORATION.

It is now necessary to consider what is ordinarily known as evaporation of a liquid. Although at first sight it appears very different from the vaporization just discussed, it is in reality the same thing. *Vaporization from the surface of a liquid above which is the gas of another substance does not take place under the pressure of that gas, but under the pressure of any vapor of the evaporating liquid which may be present and be mixed with the gas.* Thus water in a vessel open at the top will evaporate or vaporize in the same way and with the same absorption of heat, and in the same quantity, if it be exposed to still air or other similar gas, or be exposed to a space devoid of air or other gas. The pressure under which evaporation takes place is that of the water vapor in the space above the surface of the liquid, and if there happens to be air in that space the phenomenon of evaporation is not altered. For very exact

physical work this statement must be modified to take account of certain variations introduced by very minute molecular attractions between different gases and vapors, but for the most exact engineering work the law may be stated:

*Evaporation from the surface of a liquid in contact with a gas or gases with which the liquid or its vapor does not react chemically, is independent of the presence of that gas.*

Since the evaporation of liquid takes place under the pressure of the vapor of that liquid, the latent heat of vaporization and similar quantities must correspond to that pressure. Such heat values can easily be found for any case when a vapor table for that particular substance is at hand, because, although it is generally difficult to measure the vapor pressures, they must correspond to the temperatures of the space above the liquid. The vapor in that space must be saturated, because if superheated it would lose heat to the liquid, as previously

described. If saturated, its pressure must correspond to its temperature, and knowing the latter, the former can be found from the vapor tables. Thus, water with its surface exposed to air at a temperature of  $t^{\circ}$  F. will evaporate until the space above it contains as much water as it is capable of holding at that temperature; that is, until the volume occupied by unit weight of the vapor corresponds to the value given in the vapor tables. The water vapor must have the same temperature as the air with which it is mixed, and must have the pressure corresponding to that temperature and also contain all heat in quantities corresponding to that temperature. To find heat necessary to cause evaporation of one pound under such conditions, the temperature of the space above the liquid must be found in the steam tables, and the corresponding heat of vaporization is the value sought.

## CHAPTER VII.

### EXPANSIONS AND COMPRESSIONS OF VAPORS.

VAPORS are often used as the working substances of heat-engines and heat-pumps, because when subjected to heat treatment they undergo volume changes similar to those of gases. The laws governing the changes are, however, very different from, and not quite so simple as, those which have been formulated for the perfect gas.

#### ISOTHERMAL CHANGE OF VAPOR.

*An Isothermal or Constant Temperature Expansion of a saturated vapor must be an expansion at constant pressure because the pressure cannot change without a change of temperature.* Study of all possibilities

will reveal the fact that the only way in which a volume of saturated vapor can be increased while its pressure remains constant is by the addition of more vapor. In the case of a gas, one pound of material at a given temperature,  $T$ , can have any pressure within perfect gas limits and corresponding volume, but one pound of saturated vapor at temperature  $T$  can have only one pressure and one volume.

The process of vaporization which under constant pressure occurs at constant temperature is called the Isothermal Expansion of saturated vapor, though it might more correctly be called the Isothermal Formation of Vapor from Liquid. Corresponding liquefaction is equivalent to Isothermal Compression. The isothermal line of a saturated vapor, being a constant pressure line, must be a horizontal line on the  $PV$  diagram. It is convenient to express the isothermal by means of an equation of the form

$$PV^n = \text{constant}$$



as before, and this can be done by choosing a proper value for  $n$ . Since the line is a constant pressure line,

$$P = \text{constant}, \quad (83)$$

and a value of  $n$  must be found which will make  $V^n$  in the type form equal to unity. Obviously  $n$  must equal zero, and the Isothermal Line of Saturated Vapor is given by the equation

$$PV^0 = \text{constant}. \quad (84)$$

#### ADIABATIC CHANGE OF VAPOR.

Adiabatic changes of vapor are more complicated than isothermal changes, because, in a way, less restricted. If a saturated vapor at a certain temperature,  $T$ , and corresponding pressure,  $P$ , be allowed to expand without reception or rejection of heat, the increase of volume would be paralleled by a decrease of pressure and temperature. Decrease of temperature and pressure will, however,

cause a change in the total heat necessary to maintain the material in the form of a saturated vapor. If this heat is less for the lower pressures than for the higher initial condition, the expanded material will contain more heat than is necessary to maintain it as a saturated vapor and it will become superheated. If the total heat is greater at low than at high temperatures, the heat contained within the expanding material will not be sufficient to maintain it all in the condition of saturated vapor, and some will condense to liquid at the same temperature as the vapor, giving up its latent heat of vaporization to that material remaining in the vaporous state.

Further, if the vapor be required to do external work during the adiabatic expansion, it must supply from its own stock of heat a quantity equivalent to the work done. In the first case just considered this might be less than the heat liberated by drop of pressure, so that superheating would still take place but

not to so great a degree. It might be just equal to that liberated, under which conditions the vapor would remain dry during the entire expansion. Or it might be greater than that liberated, so that a partial condensation would have to take place to supply the extra heat needed.

To further complicate matters, any liquid which is condensed has a temperature equal to that of the vapor at the instant of its condensation. It therefore has an amount of heat associated with it equal to the heat of the liquid at that temperature. As expansion of the vapor continues, its pressure and temperature, and the heat necessary to maintain its liquid under its pressure, decrease. The liquid previously condensed will therefore have to partly re evaporate and by that means absorb its excess heat, or give it up to the expanding vapor with the same result. If the expanding vapor contains liquid before expansion starts, matters will be still further complicated by re-evaporation from that liquid.

It can readily be seen that this set of phenomena may lead to very different conditions for different vapors. The only way in which results may be arrived at is to study each vapor separately and determine physical constants to be used in its equations. Steam being a vapor which has been much used by engineers for many years, most of its constants have been accurately determined, and it will be taken as an example in illustrating the way in which the laws of adiabatic expansion are expressed.

The shape of curves representing adiabatic expansion on the  $PV$  diagram will vary with the initial quality of the vapor at the instant at which it begins to expand. The logarithmic equation

$$PV^n = \text{constant} \quad (85)$$

may be assumed for all such curves and will give sensibly correct results provided the proper values of  $n$  are used.

Zeuner found that for steam  $n$  had the following values for the initial qualities

given, when dealing with ordinary pressures:

Initial Quality.	Value of $n$ .
1.00 . . . . .	1.135
.95 . . . . .	1.130
.90 . . . . .	1.125
.85 . . . . .	1.120
.80 . . . . .	1.115
.75 . . . . .	1.110
.70 . . . . .	1.105

Which give for the value of  $n$  the following equation:

$$n = 1.035 + .1x, \quad (86)$$

where  $x$  is given in hundredths and not in per cent.

The  $T\phi$  diagram may be made to show very clearly the various changes of quality during adiabatic expansions and compressions. In Fig. 15 the line  $ab$  represents the entropy changes of water as it is heated to various temperatures. This is found by means of equation (76) by assuming the specific heat equal to unity and putting  $T_v$  equal to successively higher values corresponding to neces-

sarily higher pressures. The lines  $bc$ ,  $b'c'$ ,  $b''c''$ , etc., represent entropy changes that would take place were vaporization to occur at any of the temperatures at which they are drawn, and are obtained by equation (77). The line  $cc'''$  is drawn through the points representing the total entropy of dry and saturated vapor at different temperatures. It is obtained by adding results of equations (76) and (77).

As previously developed, if a vapor at temperature  $T_b$  have entropy as shown by point  $e$ , then it must be a wet vapor consisting of  $\frac{x}{100}$  pounds of vapor and  $\frac{1-x}{100}$  pounds of liquid. The quality  $x_e$  could be obtained by the equation

$$x_e = \frac{be}{bc}, \quad (87)$$

and this would be true for any position of the point  $e$  between the lines  $ab$  and  $cc'''$ .

Since adiabatic changes are represented



on such a diagram by vertical lines, constant entropy lines, the dotted line  $ee'''$  must represent an adiabatic expansion. It can be readily seen that in the case of water vapor, for which this diagram was drawn, the quality  $\frac{be}{bc}$ ,  $\frac{b'e'}{b'c''}$ ,  $\frac{b''e''}{b''c'''}$ , etc., decreases as expansion continues. If expansion had started at  $f$ , about half-way between  $b$  and  $c$ , representing a quality of 50%, the diagram shows that the quality would have remained nearly constant. Expansion starting at  $g$ , with quality lower than 50%, shows an improvement in quality as expansion proceeds. These results are of course true for steam only; to determine corresponding laws for other vapors, similar diagrams would have to be constructed for them and their laws developed individually. This serves, however, to indicate the very convenient and simple method which the conception of entropy gives for determining laws of materials of very complex behavior.

## CHAPTER VIII.

### VAPOR CYCLES.

As in the case of gas-engines, the Carnot cycle is used as the standard of excellence for vapor engines. Due, however, to the peculiar properties of vapors, the shape of the Carnot cycle for such working substances is different from that already studied. Remembering that it consists of two isothermals crossed by two adiabatics, and that isothermals for vapors are constant pressure processes, the reason for the main difference in shape is apparent.

#### CARNOT CYCLE FOR VAPOR.

If, in Fig. 16, the volume  $V_a$  be taken to represent that of one pound of mixed

liquid and vapor at pressure  $P_a$ , the addition of heat will cause further vaporization at constant temperature. This will be an isothermal expansion continuing to

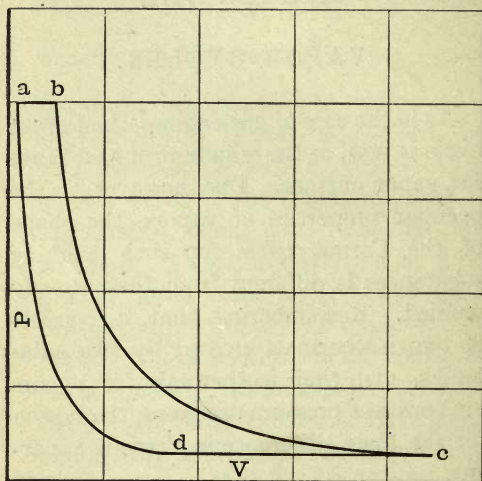


FIG. 16.

some point,  $b$ , with partial or total vaporization. Adiabatic expansion will then take place according to the law

$$PV^n = \text{constant},$$

but  $n$  will have a value dependent upon the initial quality at  $b$ . Thus with steam, if the quality at  $b$  were 100%, Zeuner's equation of  $bc$  would be

$$PV^{1.135} = \text{constant},$$

and if  $x_b$  were equal to 75%,

$$PV^{1.110} = \text{constant}$$

would give the line  $bc$ .

The line  $cd$  represents partial condensation until the volume  $V_a$  is reached, when adiabatic compression will bring it back to the condition of mixed vapor and liquid at pressure  $P_a$  and volume  $V_a$ .

The heat supplied along  $ab$  will be the difference between total heat in the material at  $a$  and  $b$ . Thus,

$$\begin{aligned} Q_1 &= (x_b r_b + q_b) - (x_a r_a + q_a) = x_b r_b - x_a r_a \\ &= r_a (x_b - x_a). \end{aligned} \quad (88)$$

Similarly the heat rejected along  $cd$  will be the amount of latent heat given up, and since there may be any quality at  $c$

and any other quality less than that at  $d$ , the expression is similar to the above:

$$Q_2 = x_c r_c - x_d r_d = r_c (x_c - x_d). \quad (89)$$

The work done during the isothermal expansions and compressions is given by the type formula of equation (6), and that during adiabatic changes by the first part of equation (40). The first part of the latter equation was developed without making use of properties peculiar to perfect gases and will hold for any material for which it can be said that  $PV^n$  is constant during an adiabatic change.

A table can then be constructed similar to that used in the case of the Carnot cycle, with gas for working substance, as follows:

Line.	Heat Received.	Work Done.
$ab$	$+r_a(x_b - x_a)$	$+P_a(V_b - V_a)$
$bc$	0	$+\frac{P_b V_b - P_c V_c}{n-1}$
$cd$	$-r_c(x_c - x_d)$	$-P_c(V_c - V_d)$
$da$	0	$-\frac{P_a V_a - P_d V_d}{n-1}$

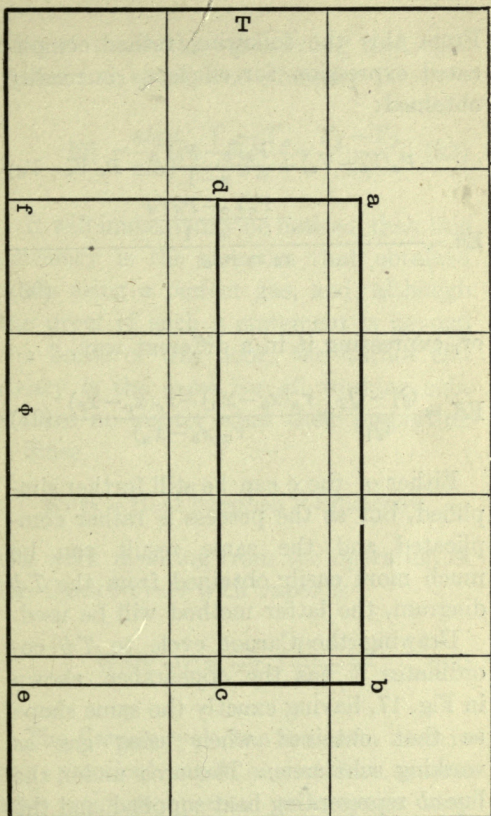


FIG. 17.



From this the following rather complicated expression for efficiency is readily obtained:

$$\text{Eff.} = \frac{P_a(V_b - V_a) + \frac{P_b V_b - P_c V_c}{n-1} - P_c(V_c - V_d) - \frac{P_a V_a - P_d V_d}{n-1}}{r_a(x_b - x_a)} \quad (90)$$

or, expressing it in a different way,

$$\text{Eff.} = \frac{Q_1 - Q_2}{Q_1} = \frac{r_a(x_b - x_a) - r_c(x_c - x_d)}{r_a(x_b - x_a)}. \quad (91)$$

Either of these can be still further simplified, but as the process is rather complicated and the same result can be much more easily obtained from the  $T\phi$  diagram, the latter method will be used.

Drawing the Carnot cycle to  $T\phi$  coordinates it has the appearance shown in Fig. 17, having exactly the same shape as that obtained when using gas as working substance. The area under the line  $ab$  representing heat supplied, and the

area of the cycle representing heat converted into work, the efficiency

$$\text{Eff.} = \frac{abcd}{abef} = \frac{T_a - T_c}{T_a} = \frac{T_1 - T_2}{T_1}. \quad (92)$$

It will immediately be noticed that this efficiency is the same as that obtained when using a perfect gas, and, although the proof of such a statement is beyond the limits of this book, the Carnot efficiency is the same for all working substances no matter what their properties.

Since

$$\text{Work} = \text{Heat supplied} \times \text{Efficiency},$$

the work resulting from the operation of the Carnot cycle with vapor is

$$\text{Work} = r(x_b - x_a) \frac{T_1 - T_2}{T_1}. \quad (93)$$

The Carnot cycle has not been used in any practical vapor engine, but several such engines operate with cycles very

similar to that of Carnot. The so-called "Clausius Cycle," which is that of the modern steam-turbine, is an illustration of a practical cycle obtained by slight modification of Carnot's.

#### CLAUSIUS CYCLE.

Drawn on the  $PV$  diagram, this cycle has the shape shown in Fig. 18. Assume the volume,  $V_a$ , to represent that of one pound of liquid at the temperature of vaporization, corresponding to the pressure  $P_a$ . The addition of heat will cause isothermal vaporization or expansion until some point,  $b$ , is reached, at which time the vapor will have a quality,  $x_b$ , equal to or less than unity. Adiabatic expansion will then bring the material to  $V_c$  with a pressure,  $P_c$ , at which point condensation may be made use of to bring the material back to the liquid state at the same pressure,  $P_c$  or  $P_a$ , and with volume,  $V_d$ , practically equal to  $V_a$ , since the expansion of liquids through

ordinary temperature ranges is negligible when compared to the vapor volume changes. The line  $da$  may then be

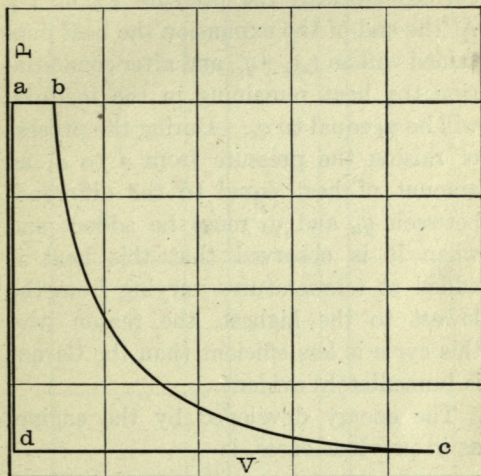


FIG. 18.

assumed a constant volume or vertical line, and represents the raising of pressure and temperature of the liquid from conditions at  $d$  to those at  $a$ .

The heat above  $32^{\circ}$  F. contained in the

liquid at  $V_a$  will be  $q_a$ , corresponding to the pressure  $P_a$ . That in the material at  $b$  will be  $q_a + x_b r_b$ , and  $r_b$  will of course correspond with the pressure  $P_b$  or  $P_a$ . At the end of the expansion the heat contained will be  $x_c r_c + q_c$ , and after condensation the heat remaining in the material will be  $q_d$  equal to  $q_c$ . During the process of raising the pressure from  $d$  to  $a$ , an amount of heat equal to the difference between  $q_a$  and  $q_d$  must be added, and when it is observed that this heat is added at temperatures varying from the lowest to the highest, the reason why this cycle is less efficient than the Carnot is immediately evident.

The energy developed by the engine, as in previous cases, is

$$E = Q_1 - Q_2 = (q_a - q_d) + x_b r_b - x_c r_c, \quad (94)$$

and the efficiency of the engine is

$$\text{Eff.} = \frac{Q_1 - Q_2}{Q_1} = \frac{(q_a - q_d) + x_b r_b - x_c r_c}{(q_a - q_d) + x_b r_b}. \quad (95)$$

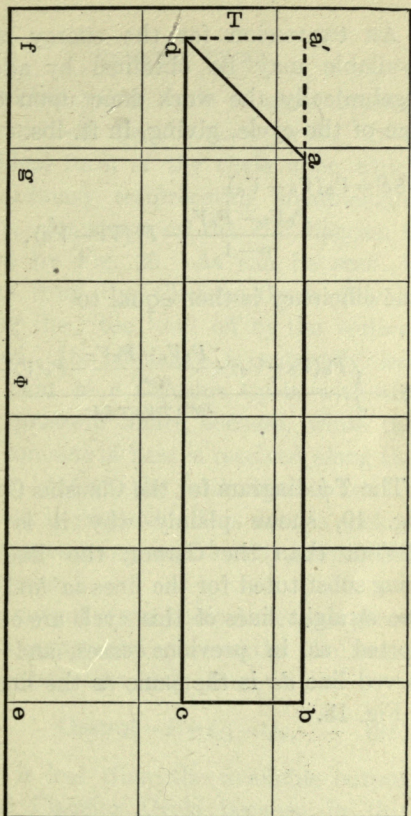


FIG. 15.



An expression for the energy made available may be obtained by adding algebraically the work done upon each line of the cycle, giving, in ft.-lbs.

$$778E = P_a(V_b - V_a) + \frac{P_bV_b - P_cV_c}{n-1} - P_c(V_c - V_d). \quad (96)$$

The efficiency is then equal to

$$\text{Eff.} = \frac{1}{J} \frac{P_a(V_b - V_a) + \frac{P_bV_b - P_cV_c}{n-1} - P_c(V_c - V_d)}{x_b r_b + q_a - q_d} \quad (97)$$

The  $T\phi$  diagram for the Clausius Cycle, Fig. 19, shows plainly why it is less efficient than the Carnot, the line  $da$  being substituted for the lines  $da'$  and  $a'a$ . The straight lines of this cycle are easily plotted as in previous cases, and the curved line  $da$  is the same as the line  $ab$  of Fig. 15.

## RANKINE CYCLE.

Another vapor cycle of great interest is known as the Rankine cycle. It is the ideal form of the cycle upon which the ordinary reciprocating steam-engine works. Its shape on the  $PV$  diagram is shown by Fig. 20. As can be seen, it differs from the Clausius Cycle only in having the "toe" cut off by the vertical line  $cd$ . Its efficiency is naturally less than that of a Clausius Cycle with the same pressure limits, because, while the same amount of heat is received along the lines  $ea$  and  $ab$ , the work done is less by the area beyond  $cd$ . This area is spoken of as representing work lost by incomplete expansion.

The output of mechanical energy is given by an expression of exactly the same form as equation (90); thus,

$$\text{Output} = E = Q_1 - Q_2, \quad (98)$$

which is less than the available output of the Clausius Cycle, because in this

case  $P_c$  has a greater numerical value. The efficiency is

$$\text{Eff.} = \frac{Q_1 - Q_2}{Q_1}. \quad (99)$$

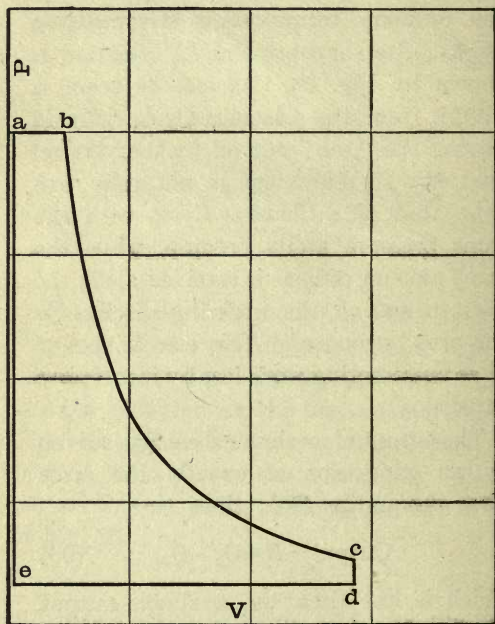


FIG. 20.

Both of these expressions give results smaller than those of the Clausius Cycle, because  $Q_2$ , the quantity of heat exhausted, is larger in the case of the Rankine for similar pressures. This is plainly evident when it is observed that at the end of the adiabatic expansion at pressure  $P_c$  condensation must take place with a rejection of heat to give the constant-volume pressure drop, while in the Turbine Cycle no heat is rejected until the pressure has dropped to the lowest point of the cycle. The difference in the value of  $Q_2$  for the two cases is plainly the difference in total heat of the vapor at pressures  $P_c$  and  $P_a$  of Fig. 20.

Expressions for work and efficiency of the Rankine Cycle similar to (92) and (93) are as follows:

$$778E = P_a(V_b - V_a) + \frac{P_b V_b - P_c V_c}{n - 1} - P_d(V_d - V_e), \quad (100)$$

and

$$\text{Eff.} = \frac{1}{J} \frac{P_a(V_b - V_a) + \frac{P_b V_b - P_c V_c}{n-1} - P_d(V_d - V_e)}{x_b r_b + (q_a - q_e)} \quad (101)$$

The  $T\phi$  diagram for this cycle having the shape drawn in Fig. 21 plainly shows the fact that it is still less efficient than that of Clausius, both being compared with the Carnot Cycle as standard.

With the exception of  $cd$ , all of the lines of this diagram are obtained exactly as are those of Fig. 19. The line  $cd$  is constructed by taking cognizance of the fact that it represents  $T\phi$  variations during a constant-volume change, as shown by  $cd$  of Fig. 20. During this volume change the pressure and temperature drop, and therefore the volume occupied by a given weight of vapor would tend to increase. Since, however, the volume is maintained constant by the piston remaining stationary at the end of the stroke, the total weight of steam remaining in the vaporous condition must be constantly

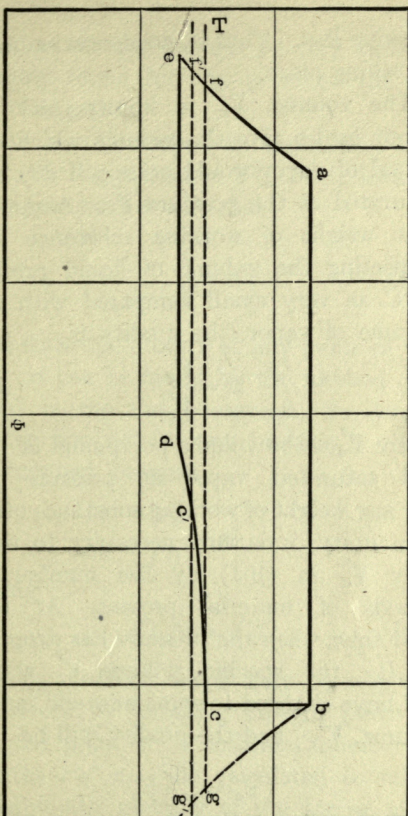


FIG. 21.



growing less. That is, condensation must be taking place.

The volume,  $V_c$ , is known, and the vapor tables give the volume which one pound of vapor would occupy if dry and saturated at the pressure  $P_c$ . Assuming unit weight of working substance and neglecting the volume of liquid present at  $C$  as very small compared with the volume of vapor, the quality is

$$x_c = \frac{V_c}{V'_c}, \quad (102)$$

where  $V'_c$  is the volume per pound of dry and saturated vapor at pressure  $P_c$ . For any weight of working substance other than unity, it is only necessary to multiply  $V'_c$  in (101) by the number of pounds of material present. At any later time, when the pressure has dropped to  $P_{c'}$ , the specific volume  $V'_c$  above will have changed to some new and larger volume,  $V'_{c'}$ , and the quality will be

$$x_{c'} = \frac{V_{c'}}{V'_{c'}},$$

so that the quality may be very approximately found for any point on the line  $cd$  of Fig. 20.

As was developed in connection with Fig. 15, the point  $c$  of Fig. 21 divides the line  $fg$  in such a way that

$$\frac{fc}{fg} = x_c; \quad (103)$$

and since the quality at any point of the line  $cd$  can be found by the method outlined in the last paragraph, the length of the line  $c'g'$  for any position is easily determined, because

$$\frac{f'c'}{f'g'} = x_{c'},$$

giving

$$f'c' = x_{c'} \cdot f'g' \quad (104)$$

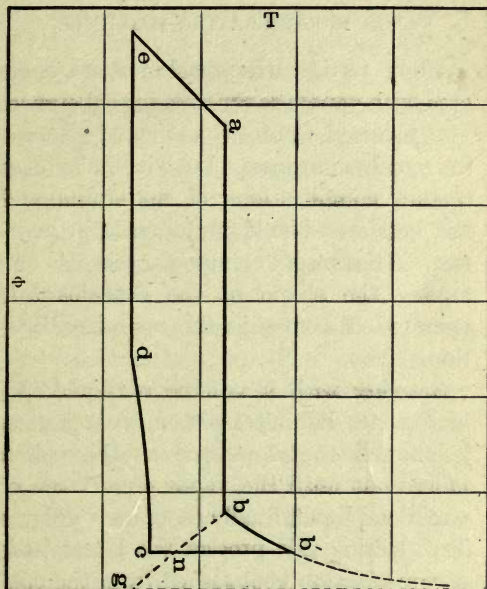
for any position which may be selected. Therefore by choosing enough positions for the point  $c'$ , a sufficient number of lengths  $c'g'$  may be calculated to make possible the plotting of the line  $cd$ , after

which the cycle continues along the same horizontal line as is used in the Clausius Cycle.

The Rankine Cycle is often modified in practice by adding more heat along the line  $ab$  than is required to form dry and saturated vapor. The result is the superheating of the material after complete evaporation, and then the adiabatic expansion starts with this superheated vapor. The  $T\phi$  diagram for such a case is shown in Fig. 22, in which, with the exception of the curve  $bb'$ , all the lines are similar to those of Fig. 21. The curve  $bb'$ , which represents the superheating of the vapor at constant pressure, is obtained by means of equation (78). The adiabatic expansion is a vertical line from the point  $b'$  down to the point which gives the desired temperature and corresponding pressure. The point,  $n$ , in which  $b'c$  crosses  $bg$  gives the temperature at which the expanding material will just reach the dry and saturated condition. If expansion continues beyond this point

the quality will constantly decrease until the partial condensation at constant volume begins at  $c$ . It is readily seen

Fig. 22.



from the dotted lines on the figure what an enormously high degree of superheat would have to be used to just give dry

and saturated steam at the end of expansion.

#### VAPOR REFRIGERATING-MACHINES.

Many refrigerating-machines are operated with vapors as the working substance. The reversed Carnot Cycle could be used for such purposes, but it introduces certain complications of apparatus and has been considered undesirable in practice. The most common cycle is one having the shape of the Clausius but operated of course in the opposite direction.

Starting with a volume of liquid,  $V_a$  in Fig. 18, behind a piston, evaporation is allowed to take place as the piston moves out until the vapor or mixture of vapor and liquid finally occupies a volume  $V_c$ . During this process the latent heat of vaporization is absorbed from the cold body, the one which is to be cooled in the ordinary practical case. The vapor, dry or wet, is then compressed adiabatically.

ically until some pressure,  $P_b$ , is reached, when condensation at constant pressure is effected. This is done by removing the latent heat of vaporization corresponding to the pressure  $P_b$  or  $P_a$ , that is, discharging it into the hot body. From  $a$  to  $d$  the pressure is dropped at practically constant volume, which means that the heat of the liquid,  $q_a - q_d$ , must be given up in some way.

Analysis of this cycle by means of the  $T\phi$  diagram given in Fig. 19 is a very simple matter.

Starting at  $d$ , heat is absorbed during the vaporization  $dc$ . The quantity of heat absorbed during this process is represented by the area  $dcef$ . Then adiabatic compression raises the temperature from  $T_c$  to  $T_b$ , after which condensation gives to the hot body the amount of heat represented by the area  $bage$ . The liquid must then be lowered in temperature from  $T_a$  to  $T_d$  and this is done by allowing it to give to the cold body an amount of heat  $adfg$ .



The result of the operation of the cycle is then the removal from the cold body of an amount of heat  $dcef$  and the return to it of an amount  $adfg$ , so that the actual refrigeration or net heat removal is the amount of heat

$$Q_2 = dcef - adfg. \quad (105)$$

This is accomplished by an expenditure of work equal in thermal units to the area  $dcbad$ .

Expressing these areas in terms of heat quantities gives

Area  $dcef$  represents  $x_c r_c$ ;

Area  $adfg$  represents  $q_a - q_d$ ;

Area  $dcbad$ , equal to  $bage + adfg - dfec$ , represents  $x_b r_b + (q_a - q_d) - x_c r_c$ .

Therefore the actual heat removed from the cold body

$$Q_2 = x_c r_c - (q_a - q_d), \quad (106)$$

and the work expended, expressed in thermal units, is

$$E = x_b r_b + q_a - q_d - x_c r_c. \quad (107)$$

The heat given to the hot body is of course the sum of heat absorbed from the cold body and work put into the mechanism, giving

$$Q_1 = Q_2 + E = x_b r_b,$$

as previously developed.

If the efficiency be taken as

$$\text{Eff.} = \frac{\text{Heat removed from cold body}}{\text{Work expended}},$$

the value for this case becomes

$$\text{Eff.} = \frac{x_c r_c - (q_a - q_d)}{x_b r_b - x_c r_c + (q_a - q_d)}, \quad (108)$$

which obviously can have any value greater or less than unity depending only upon the relative values of the heat quantities. From Fig. 19 it is evident that the steeper the line  $da$ , the greater will be the amount of heat removed for a given temperature and pressure range in the apparatus; or, the greater the

length of  $ab$  as compared with  $dc$ , the greater will be the amount of heat removed. It is therefore desirable in practice to use materials which have large latent heats of vaporization and small specific heats when in the liquid form.

Certain peculiarities of this cycle may now be noticed. Vaporization could be continued beyond  $c$  to a point  $c'$ , such that the adiabatic compression would just give dry and saturated vapor at the pressure  $P_b$ . Or vaporization could be continued to a point  $c''$ , such that adiabatic compression would superheat the material to temperature  $T_k$ , so that as the removal of heat took place the superheated vapor would first cool along a line  $Kb$  and then condense along the line  $ba$  as before. If points  $c$ ,  $c'$ , and  $c''$  be so chosen that areas  $cc'e'e$  and  $c'c''e''e'$  are equal, it can easily be seen that more area is given to the card to obtain the second than the first of the two equal areas. That means more work must be done for

a given amount of refrigerating or cooling when superheating takes place. For this reason the practical machines when operating upon this cycle always compress a wet rather than a dry vapor.

## CHAPTER IX.

### FLOW OF VAPOR.

THE formulas developed for the flow of gases from one reservoir to another were made dependent upon the truth of equation (66), which is merely another form of the following expression:

$$J(S_1 + I_1 + E_1) + \frac{V_1^2}{2g} = J(S_2 + I_2 + E_2) + \frac{V_2^2}{2g}.$$

This equation is of course equally true for vapors, being simply an algebraic statement of the fact that if no energy transfer takes place by radiation and other losses, the sum of all the energies associated with a body at the end of an operation must equal the sum of those

with which it started. Beginning with it as a basis and neglecting  $v_1$  as before,

$$\widehat{S}_1 + I_1 = q_1 + x_1 \rho_1 \quad \text{and} \quad E_1 = x_1 (APu)_1$$

and

$$S_2 + I_2 = q_2 + x_2 \rho_2 \quad \text{and} \quad E_2 = x_2 (APu)_2$$

for wet or dry saturated vapors, so that

$$\begin{aligned} \frac{v_2^2}{2g} &= J(q_1 + x_1 \rho_1 + x_1 AP_1 u_1 - q_2 - x_2 \rho_2 - x_2 P_2 u_2) \\ &= J\{(x_1 r_1 + q_1) - (x_2 r_2 + q_2)\} \\ &= J(Q_1 - Q_2) \end{aligned} \tag{109}$$

and

$$\begin{aligned} v_2 &= \sqrt{2J(Q_1 - Q_2)} \\ &= \sqrt{2J\{(x_1 r_1 + q_1) - (x_2 r_2 + q_2)\}}, \end{aligned} \tag{110}$$

where subscript (1) denotes conditions in the reservoir from which flow takes place, and subscript (2) is used to designate the conditions within the nozzle at the point at which the maximum velocity is attained.



Equation (111) can be modified to take into account superheated condition of the vapor. Thus for initial superheat but a wet final condition

$$v_2 = \sqrt{2J\{ (C_p D_1 + r_1 + q) - (x_2 r_2 + q_2) \}}, \quad (111)$$

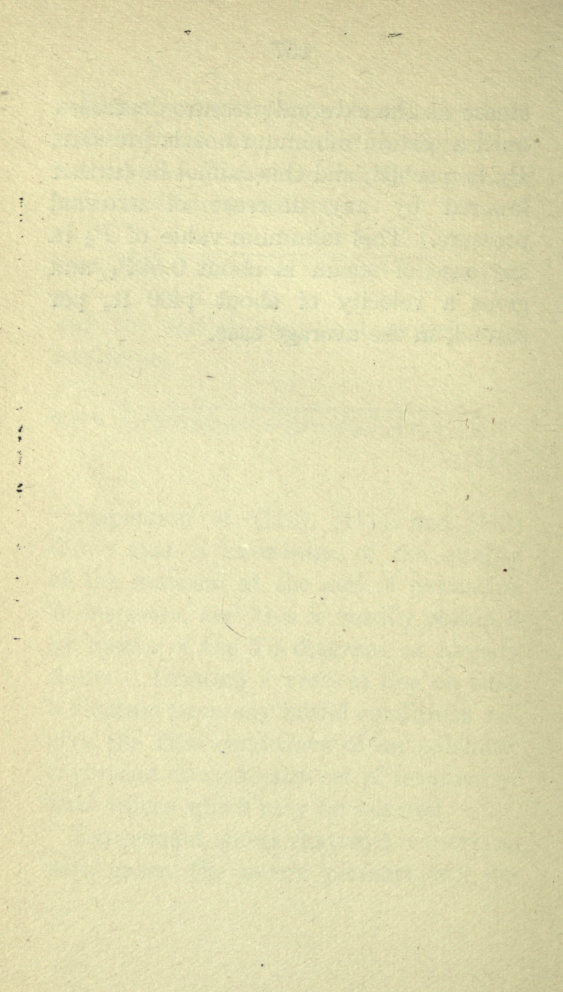
and for initial and final superheated conditions,

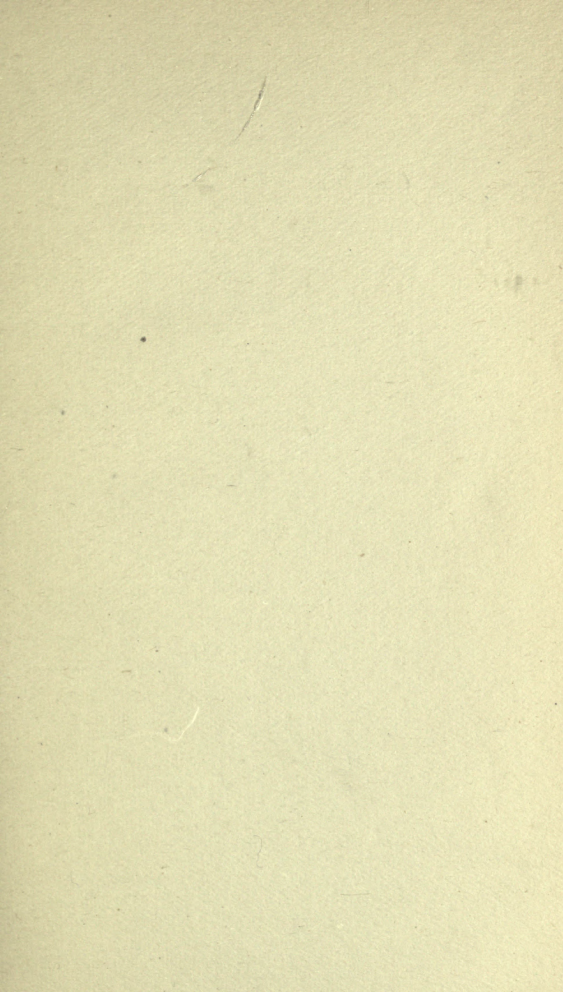
$$v_2 = \sqrt{2J\{ (C_p D_1 + r_1 + q_1) - (C_p D_2 + r_2 + q_2) \}}. \quad (112)$$

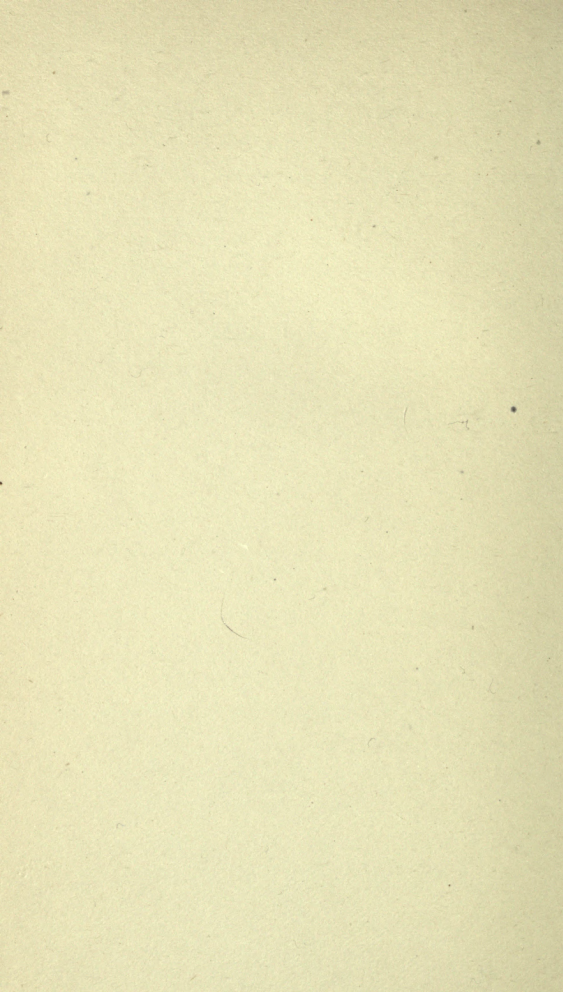
Inspection of (110), (111), and (112) shows that a knowledge of the quality of the material at the end of expansion is necessary, and this is readily obtained by means of the  $T\phi$  diagram, as already shown. Drawing a vertical line on such a diagram from any initial conditions will give the final conditions of an adiabatic expansion down to any set of terminal or final values which may be selected.

Experiment shows that with vapors, as with gases, the nozzle pressure will de-

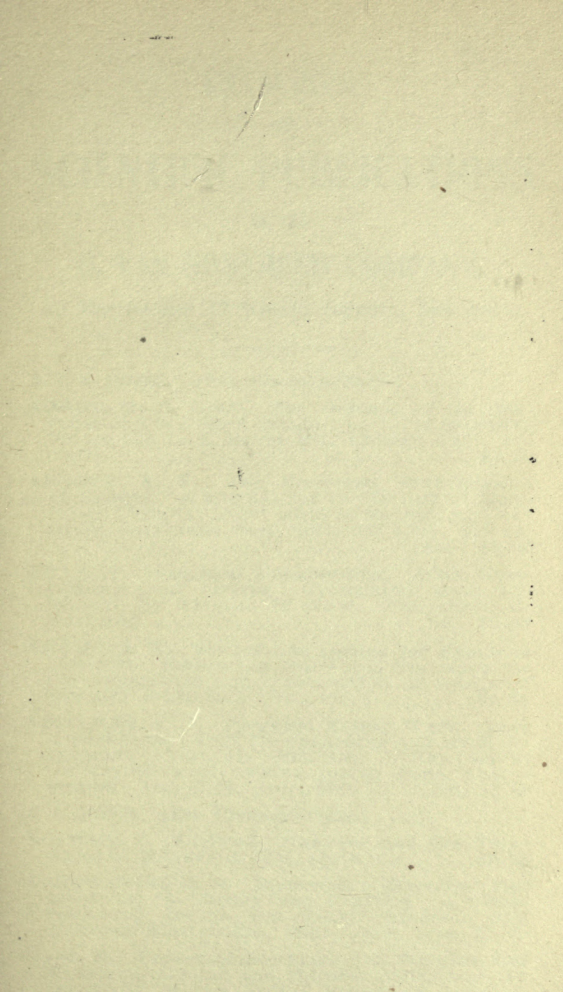
crease as the external pressure decreases, until a certain minimum nozzle pressure,  $P_2$ , is reached, and this cannot be further lowered by any decrease of external pressure. This minimum value of  $P_2$  in the case of steam is about  $0.58P_1$ , and gives a velocity of about 1400 ft. per second, in the average case.















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